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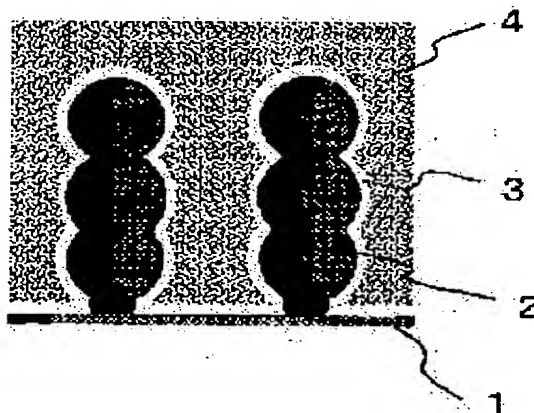
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(54) SOLID ELECTROLYTE BATTERY AND ITS MANUFACTURING METHOD

(57)Abstract:

PROBLEM TO BE SOLVED: To improve the problem in a solid electrolyte that the internal resistance is high and the charge and discharge current and charge and discharge capacity are small.

SOLUTION: The solid electrolyte battery comprises one polarity electrode made of a porous structure of active material and particle bound material, a solid electrolyte layer made of ion conductive material that has been adhered to the gap portion surface of this porous structure, and the other polarity electrode made of the other active material and a filling that have been filled in the gap portion of this porous structure. A current collector is provided to the above one polarity electrode and the other polarity electrode.



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CLAIMS

[Claim(s)]

[Claim 1] The solid electrolyte cell which has other polar lateral electrodes which consist of the unipolar lateral electrode which consists of the vesicular structure object of an active material and the particle binding matter, the solid electrolyte layer which consists of the ion conductivity matter put on the opening section front face of this vesicular structure object, and other active materials with which the opening section of this vesicular structure object was filled up and the quality of packing, and formed the charge collector in said unipolar lateral electrode and other polar lateral electrodes.

[Claim 2] The solid electrolyte cell according to claim 1 characterized by the electronic conduction nature grant matter being added by the active material of said vesicular structure object.

[Claim 3] The solid electrolyte cell according to claim 1 characterized by said particle binding matter consisting of said ion conductivity matter and/or dielectric matter.

[Claim 4] The solid electrolyte cell according to claim 1 or 3 characterized by said ion conductivity matter consisting of any one sort in glass ceramics, low melting glass, and a macromolecule, or two or more sorts.

[Claim 5] The solid electrolyte cell according to claim 3 characterized by said dielectric matter consisting of any one sort in the oxide of the metal alkoxide by low melting glass and the sol-gel method, or two or more sorts.

[Claim 6] The solid electrolyte cell according to claim 1 characterized by said particle binding matter being added by said solid electrolyte layer.

[Claim 7] The solid electrolyte cell according to claim 1 characterized by said electronic conduction nature grant matter being added by other active materials of a polar lateral electrode besides the above.

[Claim 8] The solid electrolyte cell according to claim 1 characterized by said quality of packing consisting of ion conductivity matter and/or dielectric matter.

[Claim 9] The solid electrolyte cell according to claim 8 characterized by said ion conductivity matter consisting of any one sort in glass ceramics, low melting glass, a macromolecule, gel, and nonaqueous electrolyte, or two or more sorts.

[Claim 10] The solid electrolyte cell according to claim 8 characterized by said dielectric matter consisting of any one sort in low melting glass, the oxide of the metal alkoxide by the sol-gel method, and an organic solvent, or two or more sorts.

[Claim 11] Calcinate the generation form of the active material fine particles containing a particle binder and an organic binder, and a vesicular structure object is formed. Make the solid electrolyte fine particles containing a particle binder into a mucoid with a solvent, infiltrate said vesicular structure object, calcinate, and a solid electrolyte layer is put on the opening section front face of said vesicular structure object. The manufacture approach of the calcinated solid electrolyte cell which makes a mucoid other active material fine particles which furthermore contain the quality of packing with a solvent, and fills up the opening section of said vesicular structure object with.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] Especially this invention relates to the solid electrolyte cell which attained reduction-ization of the internal resistance of an electrode and raised a charge and discharge current and charge-and-discharge capacity, and its manufacture approach about a solid electrolyte cell and its manufacture approach.

[0002]

[Description of the Prior Art] There is a thing of a liquid system or a gel system in the component using the electrochemical reaction of an electrode conventionally. For example, it sets to a nonaqueous electrolyte lithium ion battery. The laminating of the positive electrode which applied positive active material to the positive-electrode charge collector, and the negative electrode which applied the negative-electrode active material to the negative-electrode charge collector is carried out through a separator. The ion conductivity high electrolytic solution which becomes this layered product from an organic solvent and lithium salt is infiltrated. Make migration of good ion cause by the interface of an electrode and an electrolyte, and good migration of an electron and ion is made to cause with oxidization / reduction reaction in the active material of forward and the negative electrode, and the interface of the electrolytic solution, and the cell property of real use level is acquired. This has become possible by the wettability merit of a liquid system electrolyte, and high ion conductivity, and the property of real use level is acquired by the almost same reason also about the gel system electrolyte. There are the following examples as an attempt which improves the electrolyte cell of a liquid system or a gel system further.

[0003] While expanding the current capacity of a cell by forming concave heights in either [at least] a positive electrode or a negative electrode, and expanding surface area in the same nonaqueous electrolyte rechargeable battery as the above according to JP,10-223207,A (**), even if the current load characteristic of a cell is improved and overcharged or it discharges with an excessive current, it is supposed that a possibility of causing performance degradation disappeared. Moreover, by lengthening die length, the surface area which contributes to an electrochemical reaction is made to increase, and the example which improves the load characteristic of a rechargeable battery is raised at the same time according to this official report it ranks with adoption of a hypoviscosity solvent system and makes thickness of an electrode thin as a conventional example which improves a load characteristic. However, the rate of the volume which the charge collector which is not contributed to an electrochemical reaction with the increment in the die length of an electrode occupies will also increase, and the cell capacity per unit volume decreases.

[0004] According to JP,11-162519,A (**), with the conventional rechargeable lithium-ion battery, since the reaction side of the positive electrode of a pellet type and a negative electrode was restricted to the part which touches a separator, there was a problem that cannot make the whole active material contribute to a reaction, and the geometric capacity calculated from the weight of positive active material was not obtained, and the touch area of a positive electrode, a negative electrode, and a separator was not enough, and the internal resistance of a cell became

high. Then, irregularity is formed in the front face of a positive electrode and a negative electrode, and it is supposed that the touch area was made to increase and reduction of internal resistance and improvement in capacity were able to be aimed at by carrying out opposite arrangement of a positive electrode and the negative electrode through a separator so that this irregularity may gear mutually. On the other hand, the requests to the merit of safety, a miniaturization, large operating temperature limits, or user-friendliness etc. mount in recent years, consider all solid states of a component, and are giving the conventional example of a solid electrolyte.

[0005] In the layered product which has the electronic conduction body whorl which consists of an inorganic oxide, and an ion conductor layer, by contacting the interface of both layers to concave convex, the surface area of the interface is expanded, reaction effectiveness is raised, and, according to JP,5-109429,A (**), it is supposed that migration of the electron in electrode reaction and ion became good.

[0006] According to JP,9-180705,A (**), the mixed powder of an active material or an active material, and an electric conduction agent with the positive electrode and negative electrode of a lithium cell which have the solid-state-like electrode which contacted a giant-molecule solid electrolyte, a gel electrolyte, and directly Since there was a fault [contact to an active material particle, and a solid polymer electrolyte and a gel electrolyte is bad, and] that the impedance of an interface was high, While raising the adhesion of active material particles by forming the layer of wettability good polyvinyl pyridine and an electrolyte in the front face of an active material particle, and filling up the opening of this particle with an electrolyte, the capacity of a cell is raised and it is supposed that the stable cycle nature was obtained.

[0007]

[Problem(s) to be Solved by the Invention] Even if the physical properties of a metaphor electrode matrix or an electrolyte are the small solid electrolytes of ionic conductivity, this invention aims at proposing the structure of compensating this, while it improves more effectively the technical problem of conventional example **** of a liquid system, and the technical problem of conventional example **** of a solid-state system.

[0008] Although it is thought in conventional example **-* that these cross sections have the reduction effectiveness of the interfacial resistance which made irregularity the interface of electrodes 2 and 4 and an electrolyte 3, maintaining a rectangle as shown in drawing 3 , aimed at expansion of a touch area, and is proportional to expansion of a touch area in the form which carried out the laminating of the electrode and electrolyte of a sheet configuration, there is a limitation in the improvement. The purpose 1 of this invention is to exceed this limitation.

[0009] The conventional example of drawing 3 is a rectangle (the shape of a sheet, pellet type), and generally the laminating of each cross-section configuration of a positive electrode 2, the negative electrode 4, and a solid electrolyte 3 is made and carried out by a sheet forming method etc., and it uses it as a solid electrolyte cell. In drawing 3 , the electrode 2 and the electrode 4 consist of either positive-active-material fine particles or negative-electrode active material fine particles electronic conduction nature grant matter, and binding matter that consists of a solid electrolyte etc., respectively. According to drawing 3 , the touch area of the interface of electrodes 2 and 4 and a solid electrolyte 3 is proportional to distance G-H. In the above-mentioned conventional example **-*, it is what carried out surface treatment etc. at the time of sheet forming, and made the boundary of electrodes 2 and 4 and a solid electrolyte 3 a wavy line and serrate, and there is the reduction effectiveness of the interfacial resistance proportional to the increase of this segment.

[0010] Moreover, according to drawing 3 , in case ion or an electron moves between layers, there is a difference in the migration resistance by the difference in migration length. the distance to which ion moves during this period when it compares between positive active material and a negative-electrode active material (i.e., between A-B), and between C-D -- < (between A-B) (between C-D) -- it is -- migration resistance in the meantime -- < (between A-B) (between C-D) -- it is -- there is internal resistance proportional to the distance between the positive active material of arbitration and a negative-electrode active material. Generally for an electrode, the electrolyte of the thickness of drawing 3 is around 10 micrometers before and

behind 100 micrometers. Therefore, migration length is 10 micrometers to 200 micrometers, and average migration length is around 100 micrometers.

[0011] Moreover, there is resistance by the difference in the carrier of ion and an electron. Moreover, there is resistance by the difference in the electrolyte of a liquid system and a solid-state system. Ion can be easily moved in nonaqueous electrolyte at high speed, although it is difficult for size and mass to be large and to move generally in a solid-state at high speed compared with an electron.

[0012] In the nonaqueous electrolyte which consists of an organic solvent containing lithium salt, ionic conductivity can disregard very small $1 \times 10^{-2} - 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ and the resistance difference it is large and according to the difference in such migration length. On the other hand, in a solid electrolyte 3, generally, $1 \times 10^{-4} - 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$ and resistance it is small and according to such migration length have large ionic conductivity, and the resistance difference by the difference in migration length also has it. [very large] On the other hand, C-E and D-F differs in the distance which, as for an electron, an electron moves to a charge collector from each electrode from A-E and B-F, and it is [the passing speed of electronic original of resistance according to early and this migration length compared with the passing speed of ion is small, and] small. [of the resistance difference by the difference in migration length]

[0013] A resistance if daily dose of electronic conduction nature grant matter is reduced in order to increase daily dose of active material [in / for example / electrodes 2 and 4], electronic conduction nature grant matter will become inadequate, turbulence occurs in microstructure in electrode 2 and 4, and whenever [electronic conduction] becomes small, and according to electronic migration length becomes large, and according to the difference of migration length resistance difference also becomes large, and it becomes impossible however, to ignore.

[0014] In conventional example **, reduction-ization of contact interface (so-called grain boundary) resistance with electrode active material fine particles and the solid electrolyte of the shape of a matrix surrounding this is attained. Other examples which reduce this grain boundary resistance are raised with this invention.

[0015] The important technical problem which is not in conventional example **--** occurs. It is that the bulk resistor of the electrode matrix surrounding the electrode active material fine particles which consisted of solid electrolytes, and a solid electrolyte layer is large. This originates in the solid electrolyte of ionic conductivity being small compared with the electrolyte of a liquid system or a gel system. For this reason, the internal resistance proportional to the migration length of the ion from positive-active-material fine particles to negative-electrode active material fine particles appeared greatly, and originated in this resistance, it was restricted to the field to which the reaction side of a positive electrode and the negative electrode touches a solid electrolyte, the utilization factor of an active material fell [the charge and discharge current consistency became small, or], and there was a problem that charge-and-discharge capacity became small. The purpose 2 of this invention is to solve this problem.

[0016] For the purpose 1, since migration of ion takes place also by the interface of an electrode and an electrolyte layer, it should just make surface area of this interface as large beyond the conventional example as possible. For the purpose 2, since the chemical reaction (oxidation reduction reaction) which is the property of an electrochemistry component occurs by the interface of active material fine particles and the electrolyte surrounding this, it should just shorten migration length of the ion from positive-active-material fine particles to negative-electrode active material fine particles as much as possible that what is necessary is just to enlarge surface area of this grain boundary as much as possible for mentioning reaction effectiveness.

[0017] the electrolyte with which this invention used the electrochemical reaction of an electrode -- solid Io -- it is in reducing migration resistance of a NIKUSU component and the ion from the positive-active-material fine particles which more specifically present the new structure of a solid electrolyte cell, and originate in the interfacial resistance of the purposes 1 and 2, i.e., an electrode, and a solid electrolyte layer, and an electrolytic bulk resistor by this to negative-electrode active material fine particles. And it is also going to reduce migration resistance of the electron from positive-electrode (or negative electrode) active material fine

particles to a positive-electrode (or negative electrode) charge collector additionally. The final purpose of this invention is by attaining reduction-ization of such internal resistance to raise the charge and discharge current and charge-and-discharge capacity of a solid electrolyte cell.

[0018]

[Means for Solving the Problem] The solid electrolyte cell concerning claim 1 has other polar lateral electrodes which consist of the unipolar lateral electrode which consists of the vesicular structure object of an active material and the particle binding matter, the solid electrolyte layer which consists of the ion conductivity matter put on the opening section front face of this vesicular structure object, and other active materials with which the opening section of this vesicular structure object was filled up and the quality of packing, and formed the charge collector in said unipolar lateral electrode and other polar lateral electrodes.

[0019] It is desirable for the electronic conduction nature grant matter to be added by the active material of said vesicular structure object in the above-mentioned solid electrolyte cell.

[0020] It is desirable for said particle binding matter to consist of said ion conductivity matter and/or dielectric matter in the above-mentioned solid electrolyte cell.

[0021] It is desirable for said ion conductivity matter to consist of any one sort in glass ceramics, low melting glass, and a macromolecule or two or more sorts in the above-mentioned solid electrolyte cell.

[0022] It is desirable for said particle binding matter to be added by said solid electrolyte layer in the above-mentioned solid electrolyte cell.

[0023] It is desirable for said electronic conduction nature grant matter to be added by other active materials of a polar lateral electrode besides the above in the above-mentioned solid electrolyte cell.

[0024] It is desirable for said quality of packing to consist of ion conductivity matter and/or dielectric matter in the above-mentioned solid electrolyte cell.

[0025] moreover, by the manufacture approach of the solid electrolyte cell concerning claim 11 Calcinate the generation form of the active material fine particles containing a particle binder and an organic binder, and a vesicular structure object is formed. Make the solid electrolyte fine particles containing a particle binder into a mucoid with a solvent, infiltrate said vesicular structure object, calcinate, and a solid electrolyte layer is put on the opening section front face of said vesicular structure object. Other active material fine particles which furthermore contain the quality of packing are made into a mucoid with a solvent, and it is characterized by filling up the opening section of said vesicular structure object, and calcinating.

[0026]

[Embodiment of the Invention] Drawing 1 is the mimetic diagram showing the cross section of the solid electrolyte cell concerning this invention. Drawing 2 is drawing which expanded the important section of the cross section of drawing 1.

[0027] In drawing 1 and drawing 2, 1 is a charge collector and 2 is a charge collector the electrode and polarity side (a negative electrode or positive electrode) of others [5] a unipolarity side (forward or negative) a unipolarity side (a positive electrode or negative electrode) the electrode and polarity side (negative or forward) of others [3 / 4 / a solid electrolyte layer and]. Hereafter, other forward and polarities side is explained for a unipolarity side as negative for convenience. The differences between drawing 1 and drawing 2, and drawing 3 are a positive electrode, the negative electrode, and the cross-section configuration of a solid electrolyte.

[0028] In drawing 1, the cross-section configuration of the positive electrode 2 which made the vesicular structure object the frame is typically illustrated to the grape tufted one of the assembly of a large particle, and the cross-section configuration of the negative electrode 4 is the assembly of a small particle. It is illustrating typically so that the clearance between above-mentioned grape tufted may be filled, and the cross-section configuration of a solid electrolyte 3 has accomplished thin fixed thickness on the boundary of the cross section of these positive electrodes 2, and the cross section of the negative electrode 4, and it is the thin layer typically illustrated to drawing 2 which is the important section enlarged drawing of drawing 1.

[0029] The grape tufted positive electrode 2 is switch-on in electronic conduction nature and

ion conductivity. Electronically, it is in a connection condition also at a charge collector 1. Moreover, although the grape tufted cross-section section 6 isolated to drawing 1 is illustrated, it is connected with the grape tufted positive electrode 2 at other cut ends, and all are some porous body electrodes.

[0030] In drawing 1, a positive electrode 2 consists of positive-active-material fine particles and particle binding matter, in addition may also contain the electronic conduction nature matter. Moreover, a solid electrolyte 3 has ion conductivity and consists of particle binding matter etc. Moreover, the negative electrode 4 is constituted negative-electrode active material fine particles and qualitatively of packing, in addition may also contain the electronic conduction nature matter. Thickness except the charge collectors 1 and 5 of drawing 1 is made into 200-micrometer order in the semantics which holds an active material almost equivalent to drawing 3.

[0031] If the migration length between a positive electrode 2 and a negative electrode 4 is considered about each of ion and an electron based on this drawing 1, also in the part of an electrode 2 and 4 throats, it is clearer than drawing that it is magnitude extent of the grape tufted fine-particles grain of the positive electrode 2 which is a vesicular structure object or magnitude extent of the fine-particles grain of the negative electrode 4 with which it filled up so that a porous body might be buried, i.e., at most several micrometers.

[0032] If it is small migration length of this level, even if the metaphor electrode 2, and the ion conductivity in four and electronic conduction nature are small, the ion resistance and electronic resistance resulting from migration length are very small. Moreover, the thickness of a solid electrolyte 3 is also thin and the ion resistance in a solid electrolyte 3 is also small. Furthermore, if an electrode 2 and electronic conduction nature high within four are secured also about the electronic conduction nature accompanying the migration length of electrodes 2 and 4 and charge collectors 1 and 5, electronic resistance can be disregarded small. That is, since about double figures migration length is small made according to this invention even if the resistivity of ion or an electron compares compared with a liquid system and a solid-state system is large double figures, migration resistance of ion or an electron is made to the almost same resistance. Moreover, the area of the interface of electrodes 2 and 4 and a solid electrolyte 3 increases by leaps and bounds so that it can guess more easily than drawing 1. Therefore, resistance of the interface of electrodes 2 and 4 and a solid electrolyte 3 can also decrease sharply.

[0033] Thus, even if the thickness of electrodes 2 and 4 and a solid electrolyte 3 is thin respectively, and is uniform in a stratification plane with a large charge and discharge current consistency and metaphor current density is small, by the large stratification plane, the charge and discharge current consistency (this consistency is per [to charge collectors 1 and 5] unit area) as the whole current becomes large, and charge-and-discharge capacity also becomes large.

[0034] There are various approaches in forming the solid electrolyte cell of structure as shown in drawing 1 and drawing 2.

[0035] First, the electrode 2 of the vesicular structure object which consists of positive active material is produced. The fine particles of positive active material are bound with the particle binding matter, and the porous body used as the frame of a solid electrolyte cell is produced. Although 50% or less of the filling factor of a porous body is desirable from the utilization factor of a charge-and-discharge operation, it is not limited to this.

[0036] as particle binding matter, the ion conductivity matter, the lithium content matter, the dielectric matter, etc. are desirable, for example, the oxide of the metal alkoxide by the sol-gel method etc. is mentioned, and the low melting glass of the presentation containing lithiums, such as a crystallization glass [which has ion conductivity], amorphous glass, and organic giant molecule, etc. is independent in these -- or it can mix and use. For example, ion conductivity glass ceramics have the high melting point, and since there is a possibility of destroying the crystal structure of an active material and causing trouble to an oxidation reduction reaction when the temperature of active material fine particles goes up by high binding temperature, it is good to mix and use the low melting glass which can more specifically perform low-temperature binding as particle binding matter.

[0037] Moreover, when an active material particle is bound with the particle binding matter, and it considers as a porous body, and the electronic conduction nature of this porous body is small and inadequate, if an electronic conduction nature grant matter particle is mixed and used for an active material particle, electronic conduction nature will be made highly and electronic migration resistance can be performed small.

[0038] This vesicular structure object makes active material fine particles, particle binding matter fine particles, etc. a mucoïd (the shape of a slurry) with a solvent, an organic binder, etc., with a doctor blade, perform sheet forming etc., and makes it dry and sinter, and can create them. The organic binder used for shaping can be calcinated and flown, and the opening of a vesicular structure object can be made. There are print processes and dip coating other than a doctor blade method. Moreover, this vesicular structure object mixes active material fine particles etc. with a metal alkoxide, presupposes that it is liquefied (the shape of a slurry), and sheet forming etc. is performed, and it can dry and create it. At the time of desiccation, an alcoholic component can evaporate and the opening of a vesicular structure object can be made.

[0039] As particle binding matter, more specifically PVdF (polyvinylidene fluoride), PEO (polyethylene oxide), a lithium hydroxide, a lithium carbonate, Lithium content metallic oxides, such as lithium phosphate and $\text{Li}_2\text{O}-\text{SiO}_2$, and $\text{Li}_2\text{O}-\text{SiO}_2-\text{P}_2\text{O}_5$ (a metal is one or more kinds), Lithium content transition-metals oxide, such as lithium content metallic sulfide, such as lithium content metal nitrides, such as $\text{Li}_x\text{PyO}_1-\text{zNz}$, TiS_2 , or $\text{Li}_2\text{S}-\text{SiS}_2-\text{LiI}$, and a lithium titanate-acid ghost, etc. is mentioned. independent in these -- or it mixes and uses.

[0040] As an ingredient of positive active material, lithium content transition-metals oxide (transition metals are one or more kinds), such as lithium cobalt oxide, a lithium nickel oxide, a lithium manganate acid ghost, a lithium nickel manganate acid ghost, a lithium titanate-acid ghost, a lithium iron manganate acid ghost, or a lithium vanadate acid ghost, and a manganese dioxide, 5 niobium oxide, a lithium transition-metals compound nitride, TiS_2 , $\text{V}_2\text{O}_5-\text{P}_2\text{O}_5$, etc. are mentioned, for example.

[0041] Moreover, as electronic conduction nature grant matter, metallic oxides, such as carbon, acetylene black, and ITO, SnO_2 , etc. are mentioned. What is necessary is here, just to transpose to the below-mentioned negative-electrode active material, when this is a negative electrode 4 although the case where the electrode of a vesicular structure object was a positive electrode 2 was mentioned.

[0042] Next, the positive-electrode charge collector 1 is formed in the whole surface of a positive electrode 2. There are various approaches as the approach of formation. For example, it forms by forming the film of electronic conductivity of the electrode 2 of a vesicular structure object etc. in the whole surface by vacuum deposition or the sputtering method (Au, Ag, aluminum, Cu, etc.), or applying and calcinating at least, conductive paste (what mixed Au, Ag, aluminum, and Cu particle to resin) on it. As the other formation approaches, with the resin paste which mixed the particle of electronic conduction nature, the metallic foil of the shape of a sheet which consists of nickel, stainless steel, aluminum, copper, carbon, etc. is stuck on an electrode, and desiccation and baking of it may be done.

[0043] Next, the opening section front face of the acquired vesicular structure object is covered with an electrolyte, and the thin solid electrolyte layer 3 as shown in drawing 2 is formed. In order to form such a solid electrolyte layer 3, it is suitable, and what has ion conductivity like the above-mentioned particle binding matter infiltrates a vesicular structure object by making such fine particles etc. into a mucoïd (the shape of a slurry) with a solvent, and dries and creates. Moreover, the solution which can form the oxide of the metal alkoxide by the sol-gel method etc., without using the above-mentioned particle binding matter infiltrates a vesicular structure object, and it hydrolyzes on this coat, and heats and creates on it.

[0044] Next, the opening of the vesicular structure object which put the solid electrolyte 3 is filled up with a negative-electrode active material, and an electrode 4 is formed in it. The fine particles of a negative-electrode active material are infiltrated into the opening of an electrode 2 with the quality of packing, and the restoration object used as the other poles of a solid electrolyte cell is produced. Although it is desirable from the point of the volume energy density

of a charge-and-discharge operation that these structures can be formed by restoration of a restoration object so that a filling factor may become about 100%, it is not limited to this.

[0045] as restoration matter of this negative electrode, the ion conductivity matter, the lithium content matter, the dielectric matter, etc. are desirable, dielectric matter, such as an organic solvent, etc. is mentioned and oxides of the metal alkoxide by the sol-gel method, such as low melting glass of the presentation containing lithiums, such as a crystallization glass [which specifically has ion conductivity], amorphous glass, and organic giant molecule, a gel electrolyte, and nonaqueous electrolyte, etc. are independent in these -- or it can mix and use. For example, ion conductivity glass ceramics have the high melting point, and since there is a possibility of destroying the crystal structure of an active material and causing trouble to an oxidation reduction reaction when the temperature of active material fine particles goes up by high binding temperature, it is good to mix and use the organic macromolecule which can more specifically perform low-temperature binding as quality of packing.

[0046] Moreover, if an electronic conduction nature grant matter particle is mixed and used for an active material particle when an active material particle is bound qualitatively of packing, and it considers as a restoration object, and the electronic conduction nature of this restoration object is small and inadequate, electronic conduction nature can be improved and electronic migration resistance can be made small.

[0047] Active material fine particles, quality of packing, etc. can be made liquefied (the shape of a slurry) with a solvent etc., this packing structure is infiltrated, and it dries to a porous body, and it can calcinate and create them to it. The smaller one of the size of the sinking-in particle which forms an electrode 4 is better than the size of the frame particle which forms an electrode 2 from a viewpoint of raising the amount of sinking in (filling factor). Moreover, it can form at low temperature more and the way of the quality of packing which does not produce the evaporation matter at the time of baking can raise a filling factor.

[0048] By the way, as an ingredient of a negative-electrode active material, lithium content transition-metals oxide (transition metals are one or more kinds), such as carbon system ingredients, such as a metal lithium, a lithium alloy, a graphite, and corks, a lithium titanate-acid ghost, lithium cobalt oxide, a lithium nickel oxide, a lithium manganate acid ghost, a lithium nickel manganate acid ghost, a lithium iron manganate acid ghost, or a lithium vanadate acid ghost, a manganese dioxide, 5 niobium oxide, a lithium transition-metals compound nitride, or TiS_2 is mentioned, for example.

[0049] Moreover, as electronic conduction nature grant matter used with a negative-electrode active material, metallic oxides, such as carbon, acetylene black, and ITO, SnO , etc. are mentioned. What is necessary is just to replace a negative-electrode active material at the above-mentioned positive active material in the case of a positive electrode, although the case where the electrode of packing structure was a negative electrode was mentioned here.

[0050] Next, the negative-electrode (or positive electrode) charge collector 5 is formed in the cell cell confrontation of a charge collector 1. Various approaches can be considered as the formation approach and it is not limited to the following forming methods. For example, the film of electronic conductivity etc. is formed in the restoration electrode 4 by vacuum deposition, the sputtering method, spreading, baking of conductive paste, etc.

[0051] In drawing 2, an interlayer may be prepared between an electrode 2, a solid electrolyte 3, and an electrode 4 and a solid electrolyte 3, as for such an interlayer, it is desirable to carry out natural formation at the reaction by process temperature, and, generally he becomes a middle presentation in presentation.

[0052] In drawing 2, by sinking nonaqueous electrolyte, such as an organic solvent or an organic solvent, and lithium salt, into all the configuration layers of an electrode 2, a solid electrolyte 3, and an electrode 4, few openings (defect) included especially in an electrode 4, a solid electrolyte 3, and an electrode 2 can be filled, and the result of still better current density is obtained. As an organic solvent, there are PC (propylene carbonate), NMP (N-methyl-2-pyrrolidone), etc. Moreover, there is LiBF_4 etc. as lithium salt which sinks in.

[0053] By carrying out the laminating of the more than one, the generation-of-electrical-energy cell of this invention can raise a generation-of-electrical-energy electrical potential difference, or

can increase a generation-of-electrical-energy current.

[0054] What is necessary is for the metal lead linked to charge collectors 1 and 5 etc. to be sufficient as these electrode terminals, and just to form a protective coat or a sheathing object in drawing 1, so that a metal lead may not be covered and the peripheral face of a solid electrolyte cell may be covered although forward and negative the electrode terminal, protective coat, or sheathing object of a solid electrolyte cell was not illustrated. Thereby, permeation of the moisture to a solid electrolyte cell etc. can be inhibited. As a protective film object, moisture-proof *****/or the sealing agents for being airtight, such as protection resin, inorganic glass, etc. for semiconductor chips, are mentioned. As a protection sheathing object, since electric insulation and fanciness are given to the outside section, the laminate film which laminated the metal sheet with insulating polyethylene terephthalate (PET), polyethylene (PE), etc. can be used.

[0055]

[Example] Flat-surface size produced the solid electrolyte cell as the cross-section configuration shows to drawing 1 by 20mmx20mm.

[0056] The low melting glass ($\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{ZnO}$) which has a lithium titanate-acid ghost ($\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}\text{O}_4]$) as a negative-electrode active material, and has lithium ion conductivity as particle binding matter to 85% of the weight was mixed 15% of the weight. To this mixture, the binder (polyvinyl butyral) was added and the paste was adjusted for toluene to the solvent. Sheet forming of the adjusted paste was carried out so that thickness might be set to 200 micrometers with a doctor blade. After drying this, it sintered at 650 degrees C and the porous body electrode was created.

[0057] Au was vapor-deposited in thickness of 0.5 micrometers with vacuum evaporation equipment, and the negative-electrode charge collector was formed in one side of this porous body electrode.

[0058] Next, toluene and viscosity control were performed and pulverized coal of low melting glass ($\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{ZnO}$) which has lithium ion conductivity as a solid electrolyte was used as the solution. After sinking in and drying this adjusted solution to a porous body electrode, it calcinated at 500 degrees C. Short prevention was performed by thinning solution viscosity and repeating coat formation several times.

[0059] Next, acetylene black was mixed as an additive which makes electronic conductivity give a lithium manganate acid ghost ($\text{Li}[\text{Li}_{0.1}\text{Mn}_{1.9}\text{O}_4]$) to 80% of the weight as positive active material, and PVdF (polyvinylidene fluoride) was mixed 10% of the weight as 10 % of the weight and particle binding matter. To this mixture, addition mixing of the NMP (N-methyl-2-pyrrolidone) was carried out, and the paste for positive-electrode formation was adjusted. The adjusted solution was sunk in and dried to the above-mentioned porous body electrode, and the restoration electrode was created.

[0060] Next, Au was vapor-deposited in thickness of 0.5 micrometers with vacuum evaporation equipment, and the positive-electrode charge collector was formed in the field of this restoration electrode.

[0061] About this cell, when asked for the discharge current consistency, 11microA/cm² was obtained. Moreover, the utilization factor of charge and discharge was 20%.

As [the object for a comparison], next an object for a comparison, by 20mmx20mm, the cross section produced [flat-surface size] the solid electrolyte cell, as shown in drawing 3.

[0062] The low melting glass ($\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{ZnO}$) which has a lithium titanate-acid ghost ($\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}\text{O}_4]$) as a negative-electrode active material, and has lithium ion conductivity as particle binding matter to 85% of the weight was mixed 15% of the weight. To this mixture, the binder (polyvinyl butyral) was added and the paste was adjusted for toluene to the solvent. Sheet forming of the adjusted paste was carried out with the doctor blade. After drying this, it sintered at 700 degrees C and the more precise negative electrode 2 whose thickness is 90 micrometers was created.

[0063] Next, the fine particles of the crystallization glass ($\text{Li}_2\text{O}-\text{SiO}_2$, $\text{Li}_2\text{O}-\text{SiO}_2-\text{P}_2\text{O}_5$) of lithium ion conductivity and the fine particles of the low melting glass ($\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{ZnO}$) which has lithium ion conductivity were adjusted with toluene as a solid electrolyte 3, and it considered

as the paste. After printing this adjusted paste to the above-mentioned negative electrode and drying, it calcinated at 550 degrees C and the solid electrolyte 3 with a thickness of 20 micrometers was obtained.

[0064] Next, after mixing acetylene black as an additive which makes electronic conductivity give a lithium manganic acid ghost ($\text{Li}[\text{Li}_{0.1}\text{Mn}_{1.9}\text{O}_4]$) to 80% of the weight as positive active material and mixing PVdF (polyvinylidene fluoride) 9% of the weight as 11 % of the weight and restoration matter, addition mixing of the NMP (N-methyl-2-pyrrolidone) was carried out, and the paste for positive-electrode formation was adjusted to this mixture. After printing the adjusted paste to the above-mentioned layered product and drying, it calcinated at 500 degrees C and the positive electrode with a thickness of 90 micrometers was created.

[0065] Next, Au was vapor-deposited in thickness of 0.5 micrometers with vacuum evaporation equipment, respectively, and the negative electrode and the positive-electrode charge collector were formed in both sides of this negative electrode and a positive electrode.

[0066] When asked for the discharge current consistency about this cell, 1microA/cm² was obtained. Moreover, the utilization factor of charge and discharge was 2%.

[0067] Conventionally, to the example of a comparison of structure, the discharge current consistency of this invention article improved from 1microA/cm² to 11microA/cm², and the utilization factor of charge and discharge improved from 2% to 20% in connection with this.

[0068]

[Effect of the Invention] As mentioned above, since it has the unipolar lateral electrode which consists of the vesicular structure object of an active material, the solid electrolyte layer which consists of the ion conductivity matter put on the opening front face of this vesicular structure object, and other polar lateral electrodes which consist of other active materials with which the opening of this vesicular structure object was filled up according to the solid electrolyte cell concerning claim 1, the high internal resistance of a solid electrolyte can be mitigated remarkably, and a charge and discharge current and charge-and-discharge capacity can be raised.

[0069] Moreover, according to the manufacture approach of the solid electrolyte cell concerning claim 11, calcinate the generation form of the active material fine particles containing a particle binder and an organic binder, and a vesicular structure object is formed: Make the solid electrolyte fine particles containing a particle binder into a mucoid with a solvent, infiltrate the above-mentioned vesicular structure object, calcinate, and a solid electrolyte layer is put on the opening section front face of a vesicular structure object. Since other active material fine particles which furthermore contain the quality of packing are made into a mucoid, and the opening of the above-mentioned vesicular structure object is filled up with them and they are calcinated with a solvent, the high internal resistance of a solid electrolyte is mitigated remarkably, and the solid electrolyte cell which raised a charge and discharge current and charge-and-discharge capacity can be manufactured easily.

[Translation done.]

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TECHNICAL FIELD

[Field of the Invention] Especially this invention relates to the solid electrolyte cell which attained reduction-ization of the internal resistance of an electrode and raised a charge and discharge current and charge-and-discharge capacity, and its manufacture approach about a solid electrolyte cell and its manufacture approach.

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PRIOR ART

[Description of the Prior Art] There is a thing of a liquid system or a gel system in the component using the electrochemical reaction of an electrode conventionally. For example, it sets to a nonaqueous electrolyte lithium ion battery. The laminating of the positive electrode which applied positive active material to the positive-electrode charge collector, and the negative electrode which applied the negative-electrode active material to the negative-electrode charge collector is carried out through a separator. The ion conductivity high electrolytic solution which becomes this layered product from an organic solvent and lithium salt is infiltrated. Make migration of good ion cause by the interface of an electrode and an electrolyte, and good migration of an electron and ion is made to cause with oxidization / reduction reaction in the active material of forward and the negative electrode, and the interface of the electrolytic solution, and the cell property of real use level is acquired. This has become possible by the wettability merit of a liquid system electrolyte, and high ion conductivity, and the property of real use level is acquired by the almost same reason also about the gel system electrolyte. There are the following examples as an attempt which improves the electrolyte cell of a liquid system or a gel system further.

[0003] While expanding the current capacity of a cell by forming concave heights in either [at least] a positive electrode or a negative electrode, and expanding surface area in the same nonaqueous electrolyte rechargeable battery as the above according to JP,10-223207,A (**), even if the current load characteristic of a cell is improved and overcharged or it discharges with an excessive current, it is supposed that a possibility of causing performance degradation disappeared. Moreover, by lengthening die length, the surface area which contributes to an electrochemical reaction is made to increase, and the example which improves the load characteristic of a rechargeable battery is raised at the same time according to this official report it ranks with adoption of a hypoviscosity solvent system and makes thickness of an electrode thin as a conventional example which improves a load characteristic. However, the rate of the volume which the charge collector which is not contributed to an electrochemical reaction with the increment in the die length of an electrode occupies will also increase, and the cell capacity per unit volume decreases.

[0004] According to JP,11-162519,A (**), with the conventional rechargeable lithium-ion battery, since the reaction side of the positive electrode of a pellet type and a negative electrode was restricted to the part which touches a separator, there was a problem that cannot make the whole active material contribute to a reaction, and the geometric capacity calculated from the weight of positive active material was not obtained, and the touch area of a positive electrode, a negative electrode, and a separator was not enough, and the internal resistance of a cell became high. Then, irregularity is formed in the front face of a positive electrode and a negative electrode, and it is supposed that the touch area was made to increase and reduction of internal resistance and improvement in capacity were able to be aimed at by carrying out opposite arrangement of a positive electrode and the negative electrode through a separator so that this irregularity may gear mutually. On the other hand, the requests to the merit of safety, a miniaturization, large operating temperature limits, or user-friendliness etc. mount in recent years, consider all solid states of a component, and are giving the conventional example of a

solid electrolyte.

[0005] In the layered product which has the electronic conduction body whorl which consists of an inorganic oxide, and an ion conductor layer, by contacting the interface of both layers to concave convex, the surface area of the interface is expanded, reaction effectiveness is raised, and, according to JP,5-109429,A (**), it is supposed that migration of the electron in electrode reaction and ion became good.

[0006] According to JP,9-180705,A (**), the mixed powder of an active material or an active material, and an electric conduction agent with the positive electrode and negative electrode of a lithium cell which have the solid-state-like electrode which contacted a giant-molecule solid electrolyte, a gel electrolyte, and directly Since there was a fault [contact to an active material particle, and a solid polymer electrolyte and a gel electrolyte is bad, and] that the impedance of an interface was high, While raising the adhesion of active material particles by forming the layer of wettability good polyvinyl pyridine and an electrolyte in the front face of an active material particle, and filling up the opening of this particle with an electrolyte, the capacity of a cell is raised and it is supposed that the stable cycle nature was obtained.

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EFFECT OF THE INVENTION

[Effect of the Invention] As mentioned above, since it has the unipolar lateral electrode which consists of the vesicular structure object of an active material, the solid electrolyte layer which consists of the ion conductivity matter put on the opening front face of this vesicular structure object, and other polar lateral electrodes which consist of other active materials with which the opening of this vesicular structure object was filled up according to the solid electrolyte cell concerning claim 1, the high internal resistance of a solid electrolyte can be mitigated remarkably, and a charge and discharge current and charge-and-discharge capacity can be raised.

[0069] Moreover, according to the manufacture approach of the solid electrolyte cell concerning claim 11, calcinate the generation form of the active material fine particles containing a particle binder and an organic binder, and a vesicular structure object is formed. Make the solid electrolyte fine particles containing a particle binder into a mucoid with a solvent, infiltrate the above-mentioned vesicular structure object, calcinate, and a solid electrolyte layer is put on the opening section front face of a vesicular structure object. Since other active material fine particles which furthermore contain the quality of packing are made into a mucoid, and the opening of the above-mentioned vesicular structure object is filled up with them and they are calcinated with a solvent, the high internal resistance of a solid electrolyte is mitigated remarkably, and the solid electrolyte cell which raised a charge and discharge current and charge-and-discharge capacity can be manufactured easily.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] Even if the physical properties of a metaphor electrode matrix or an electrolyte are the small solid electrolytes of ionic conductivity, this invention aims at proposing the structure of compensating this, while it improves more effectively the technical problem of conventional example **** of a liquid system, and the technical problem of conventional example **** of a solid-state system.

[0008] Although it is thought in conventional example **-* that these cross sections have the reduction effectiveness of the interfacial resistance which made irregularity the interface of electrodes 2 and 4 and an electrolyte 3, maintaining a rectangle as shown in drawing 3, aimed at expansion of a touch area, and is proportional to expansion of a touch area in the form which carried out the laminating of the electrode and electrolyte of a sheet configuration, there is a limitation in the improvement. The purpose 1 of this invention is to exceed this limitation.

[0009] The conventional example of drawing 3 is a rectangle (the shape of a sheet, pellet type), and generally the laminating of each cross-section configuration of a positive electrode 2, the negative electrode 4, and a solid electrolyte 3 is made and carried out by a sheet forming method etc., and it uses it as a solid electrolyte cell. In drawing 3, the electrode 2 and the electrode 4 consist of either positive-active-material fine particles or negative-electrode active material fine particles electronic conduction nature grant matter, and binding matter that consists of a solid electrolyte etc., respectively. According to drawing 3, the touch area of the interface of electrodes 2 and 4 and a solid electrolyte 3 is proportional to distance G-H. In the above-mentioned conventional example **-*, it is what carried out surface treatment etc. at the time of sheet forming, and made the boundary of electrodes 2 and 4 and a solid electrolyte 3 a wavy line and serrate, and there is the reduction effectiveness of the interfacial resistance proportional to the increase of this segment.

[0010] Moreover, according to drawing 3, in case ion or an electron moves between layers, there is a difference in the migration resistance by the difference in migration length. the distance to which ion moves during this period when it compares between positive active material and a negative-electrode active material (i.e., between A-B), and between C-D -- < (between A-B) (between C-D) -- it is -- migration resistance in the meantime -- < (between A-B) (between C-D) -- it is -- there is internal resistance proportional to the distance between the positive active material of arbitration and a negative-electrode active material. Generally for an electrode, the electrolyte of the thickness of drawing 3 is around 10 micrometers before and behind 100 micrometers. Therefore, migration length is 10 micrometers to 200 micrometers, and average migration length is around 100 micrometers.

[0011] Moreover, there is resistance by the difference in the carrier of ion and an electron. Moreover, there is resistance by the difference in the electrolyte of a liquid system and a solid-state system. Ion can be easily moved in nonaqueous electrolyte at high speed, although it is difficult for size and mass to be large and to move generally in a solid-state at high speed compared with an electron.

[0012] In the nonaqueous electrolyte which consists of an organic solvent containing lithium salt, ionic conductivity can disregard very small $1 \times 10^{-2} - 10^{-3} \text{ohm}^{-1} \text{cm}^{-1}$ and the resistance difference it is large and according to the difference in such migration length. On the other hand,

in a solid electrolyte 3, generally, $1 \times 10^{-4} - 10^{-6} \text{ohm-cm}^{-1}$ and resistance it is small and according to such migration length have large ionic conductivity, and the resistance difference by the difference in migration length also has it. [very large] On the other hand, C-E and D-F differs in the distance which, as for an electron, an electron moves to a charge collector from each electrode from A-E and B-F, and it is [the passing speed of electronic original of resistance according to early and this migration length compared with the passing speed of ion is small, and] small. [of the resistance difference by the difference in migration length]

[0013] A resistance if daily dose of electronic conduction nature grant matter is reduced in order to increase daily dose of active material [in / for example / electrodes 2 and 4], electronic conduction nature grant matter will become inadequate, turbulence occurs in microstructure in electrode 2 and 4, and whenever [electronic conduction] becomes small, and according to electronic migration length becomes large, and according to the difference of migration length resistance difference also becomes large, and it becomes impossible however, to ignore.

[0014] In conventional example **, reduction-ization of contact interface (so-called grain boundary) resistance with electrode active material fine particles and the solid electrolyte of the shape of a matrix surrounding this is attained. Other examples which reduce this grain boundary resistance are raised with this invention.

[0015] The important technical problem which is not in conventional example **--** occurs. It is that the bulk resistor of the electrode matrix surrounding the electrode active material fine particles which consisted of solid electrolytes, and a solid electrolyte layer is large. This originates in the solid electrolyte of ionic conductivity being small compared with the electrolyte of a liquid system or a gel system. For this reason, the internal resistance proportional to the migration length of the ion from positive-active-material fine particles to negative-electrode active material fine particles appeared greatly, and originated in this resistance, it was restricted to the field to which the reaction side of a positive electrode and the negative electrode touches a solid electrolyte, the utilization factor of an active material fell [the charge and discharge current consistency became small, or], and there was a problem that charge-and-discharge capacity became small. The purpose 2 of this invention is to solve this problem.

[0016] For the purpose 1, since migration of ion takes place also by the interface of an electrode and an electrolyte layer, it should just make surface area of this interface as large beyond the conventional example as possible. For the purpose 2, since the chemical reaction (oxidation reduction reaction) which is the property of an electrochemistry component occurs by the interface of active material fine particles and the electrolyte surrounding this, it should just shorten migration length of the ion from positive-active-material fine particles to negative-electrode active material fine particles as much as possible that what is necessary is just to enlarge surface area of this grain boundary as much as possible for mentioning reaction effectiveness.

[0017] the electrolyte with which this invention used the electrochemical reaction of an electrode -- solid Io -- it is in reducing migration resistance of a NIKUSU component and the ion from the positive-active-material fine particles which more specifically present the new structure of a solid electrolyte cell, and originate in the interfacial resistance of the purposes 1 and 2, i.e., an electrode, and a solid electrolyte layer, and an electrolytic bulk resistor by this to negative-electrode active material fine particles. And it is also going to reduce migration resistance of the electron from positive-electrode (or negative electrode) active material fine particles to a positive-electrode (or negative electrode) charge collector additionally. The final purpose of this invention is by attaining reduction-ization of such internal resistance to raise the charge and discharge current and charge-and-discharge capacity of a solid electrolyte cell.

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MEANS

[Means for Solving the Problem] The solid electrolyte cell concerning claim 1 has other polar lateral electrodes which consist of the unipolar lateral electrode which consists of the vesicular structure object of an active material and the particle binding matter, the solid electrolyte layer which consists of the ion conductivity matter put on the opening section front face of this vesicular structure object, and other active materials with which the opening section of this vesicular structure object was filled up and the quality of packing, and formed the charge collector in said unipolar lateral electrode and other polar lateral electrodes.

[0019] It is desirable for the electronic conduction nature grant matter to be added by the active material of said vesicular structure object in the above-mentioned solid electrolyte cell.

[0020] It is desirable for said particle binding matter to consist of said ion conductivity matter and/or dielectric matter in the above-mentioned solid electrolyte cell.

[0021] It is desirable for said ion conductivity matter to consist of any one sort in glass ceramics, low melting glass, and a macromolecule or two or more sorts in the above-mentioned solid electrolyte cell.

[0022] It is desirable for said particle binding matter to be added by said solid electrolyte layer in the above-mentioned solid electrolyte cell.

[0023] It is desirable for said electronic conduction nature grant matter to be added by other active materials of a polar lateral electrode besides the above in the above-mentioned solid electrolyte cell.

[0024] It is desirable for said quality of packing to consist of ion conductivity matter and/or dielectric matter in the above-mentioned solid electrolyte cell.

[0025] moreover, by the manufacture approach of the solid electrolyte cell concerning claim 11 Calcinate the generation form of the active material fine particles containing a particle binder and an organic binder, and a vesicular structure object is formed. Make the solid electrolyte fine particles containing a particle binder into a mucoid with a solvent, infiltrate said vesicular structure object, calcinate, and a solid electrolyte layer is put on the opening section front face of said vesicular structure object. Other active material fine particles which furthermore contain the quality of packing are made into a mucoid with a solvent, and it is characterized by filling up the opening section of said vesicular structure object, and calcinating.

[0026]

[Embodiment of the Invention] Drawing 1 is the mimetic diagram showing the cross section of the solid electrolyte cell concerning this invention. Drawing 2 is drawing which expanded the important section of the cross section of drawing 1.

[0027] In drawing 1 and drawing 2, 1 is a charge collector and 2 is a charge collector the electrode and polarity side (a negative electrode or positive electrode) of others [5] a unipolarity side (forward or negative) a unipolarity side (a positive electrode or negative electrode) the electrode and polarity side (negative or forward) of others [3 / 4 / a solid electrolyte layer and]. Hereafter, other forward and polarities side is explained for a unipolarity side as negative for convenience. The differences between drawing 1 and drawing 2, and drawing 3 are a positive electrode, the negative electrode, and the cross-section configuration of a solid electrolyte.

[0028] In drawing 1 , the cross-section configuration of the positive electrode 2 which made the vesicular structure object the frame is typically illustrated to the grape tufted one of the assembly of a large particle, and the cross-section configuration of the negative electrode 4 is the assembly of a small particle. It is illustrating typically so that the clearance between above-mentioned grape tufted may be filled, and the cross-section configuration of a solid electrolyte 3 has accomplished thin fixed thickness on the boundary of the cross section of these positive electrodes 2, and the cross section of the negative electrode 4, and it is the thin layer typically illustrated to drawing 2 which is the important section enlarged drawing of drawing 1 .

[0029] The grape tufted positive electrode 2 is switch-on in electronic conduction nature and ion conductivity. Electronically, it is in a connection condition also at a charge collector 1. Moreover, although the grape tufted cross-section section 6 isolated to drawing 1 is illustrated, it is connected with the grape tufted positive electrode 2 at other cut ends, and all are some porous body electrodes.

[0030] In drawing 1 , a positive electrode 2 consists of positive-active-material fine particles and particle binding matter, in addition may also contain the electronic conduction nature matter. Moreover, a solid electrolyte 3 has ion conductivity and consists of particle binding matter etc. Moreover, the negative electrode 4 is constituted negative-electrode active material fine particles and qualitatively of packing, in addition may also contain the electronic conduction nature matter. Thickness except the charge collectors 1 and 5 of drawing 1 is made into 200-micrometer order in the semantics which holds an active material almost equivalent to drawing 3 .

[0031] If the migration length between a positive electrode 2 and a negative electrode 4 is considered about each of ion and an electron based on this drawing 1 , also in the part of an electrode 2 and 4 throats, it is clearer than drawing that it is magnitude extent of the grape tufted fine-particles grain of the positive electrode 2 which is a vesicular structure object or magnitude extent of the fine-particles grain of the negative electrode 4 with which it filled up so that a porous body might be buried, i.e., at most several micrometers.

[0032] If it is small migration length of this level, even if the metaphor electrode 2, and the ion conductivity in four and electronic conduction nature are small, the ion resistance and electronic resistance resulting from migration length are very small. Moreover, the thickness of a solid electrolyte 3 is also thin and the ion resistance in a solid electrolyte 3 is also small. Furthermore, if an electrode 2 and electronic conduction nature high within four are secured also about the electronic conduction nature accompanying the migration length of electrodes 2 and 4 and charge collectors 1 and 5, electronic resistance can be disregarded small. That is, since about double figures migration length is small made according to this invention even if the resistivity of ion or an electron compares compared with a liquid system and a solid-state system is large double figures, migration resistance of ion or an electron is made to the almost same resistance. Moreover, the area of the interface of electrodes 2 and 4 and a solid electrolyte 3 increases by leaps and bounds so that it can guess more easily than drawing 1 . Therefore, resistance of the interface of electrodes 2 and 4 and a solid electrolyte 3 can also decrease sharply.

[0033] Thus, even if the thickness of electrodes 2 and 4 and a solid electrolyte 3 is thin respectively, and is uniform in a stratification plane with a large charge and discharge current consistency and metaphor current density is small, by the large stratification plane, the charge and discharge current consistency (this consistency is per [to charge collectors 1 and 5] unit area) as the whole current becomes large, and charge-and-discharge capacity also becomes large.

[0034] There are various approaches in forming the solid electrolyte cell of structure as shown in drawing 1 and drawing 2 .

[0035] First, the electrode 2 of the vesicular structure object which consists of positive active material is produced. The fine particles of positive active material are bound with the particle binding matter, and the porous body used as the frame of a solid electrolyte cell is produced. Although 50% or less of the filling factor of a porous body is desirable from the utilization factor of a charge-and-discharge operation, it is not limited to this.

[0036] as particle binding matter, the ion conductivity matter, the lithium content matter, the

dielectric matter, etc. are desirable, for example, the oxide of the metal alkoxide by the sol-gel method etc. is mentioned, and the low melting glass of the presentation containing lithiums, such as a crystallization glass [which has ion conductivity], amorphous glass, and organic giant molecule, etc. is independent in these -- or it can mix and use. For example, ion conductivity glass ceramics have the high melting point, and since there is a possibility of destroying the crystal structure of an active material and causing trouble to an oxidation reduction reaction when the temperature of active material fine particles goes up by high binding temperature, it is good to mix and use the low melting glass which can more specifically perform low-temperature binding as particle binding matter.

[0037] Moreover, when an active material particle is bound with the particle binding matter, and it considers as a porous body, and the electronic conduction nature of this porous body is small and inadequate, if an electronic conduction nature grant matter particle is mixed and used for an active material particle, electronic conduction nature will be made highly and electronic migration resistance can be performed small.

[0038] This vesicular structure object makes active material fine particles, particle binding matter fine particles, etc. a mucoid (the shape of a slurry) with a solvent, an organic binder, etc., with a doctor blade, perform sheet forming etc., and makes it dry and sinter, and can create them. The organic binder used for shaping can be calcinated and flown, and the opening of a vesicular structure object can be made. There are print processes and dip coating other than a doctor blade method. Moreover, this vesicular structure object mixes active material fine particles etc. with a metal alkoxide, presupposes that it is liquefied (the shape of a slurry), and sheet forming etc. is performed, and it can dry and create it. At the time of desiccation, an alcoholic component can evaporate and the opening of a vesicular structure object can be made.

[0039] As particle binding matter, more specifically PVdF (polyvinylidene fluoride), PEO (polyethylene oxide), a lithium hydroxide, a lithium carbonate, Lithium content metallic oxides, such as lithium phosphate and $\text{Li}_2\text{O}-\text{SiO}_2$, and $\text{Li}_2\text{O}-\text{SiO}_2-\text{P}_2\text{O}_5$ (a metal is one or more kinds), Lithium content transition-metals oxide, such as lithium content metallic sulfide, such as lithium content metal nitrides, such as $\text{Li}_x\text{PyO}_1-z\text{N}_z$, TiS_2 , or $\text{Li}_2\text{S}-\text{SiS}_2-\text{LiI}$, and a lithium titanate-acid ghost, etc. is mentioned. independent in these -- or it mixes and uses.

[0040] As an ingredient of positive active material, lithium content transition-metals oxide. (transition metals are one or more kinds), such as lithium cobalt oxide, a lithium nickel oxide, a lithium manganic acid ghost, a lithium nickel manganic acid ghost, a lithium titanate-acid ghost, a lithium iron manganic acid ghost, or a lithium banazin san ghost, and a manganese dioxide, 5 niobium oxide, a lithium transition-metals compound nitride, TiS_2 , $\text{V}_2\text{O}_5-\text{P}_2\text{O}_5$, etc. are mentioned, for example.

[0041] Moreover, as electronic conduction nature grant matter, metallic oxides, such as carbon, acetylene black, and ITO, SnO_2 , etc. are mentioned. What is necessary is here, just to transpose to the below-mentioned negative-electrode active material, when this is a negative electrode 4 although the case where the electrode of a vesicular structure object was a positive electrode 2 was mentioned.

[0042] Next, the positive-electrode charge collector 1 is formed in the whole surface of a positive electrode 2. There are various approaches as the approach of formation. For example, it forms by forming the film of electronic conductivity of the electrode 2 of a vesicular structure object etc. in the whole surface by vacuum deposition or the sputtering method (Au, Ag, aluminum, Cu, etc.), or applying and calcinating at least, conductive paste (what mixed Au, Ag, aluminum, and Cu particle to resin) on it. As the other formation approaches, with the resin paste which mixed the particle of electronic conduction nature, the metallic foil of the shape of a sheet which consists of nickel, stainless steel, aluminum, copper, carbon, etc. is stuck on an electrode, and desiccation and baking of it may be done.

[0043] Next, the opening section front face of the acquired vesicular structure object is covered with an electrolyte, and the thin solid electrolyte layer 3 as shown in drawing 2 is formed. In order to form such a solid electrolyte layer 3, it is suitable, and what has ion conductivity like the above-mentioned particle binding matter infiltrates a vesicular structure object by making such

fine particles etc. into a mucoid (the shape of a slurry) with a solvent, and dries and creates. Moreover, the solution which can form the oxide of the metal alkoxide by the sol-gel method etc., without using the above-mentioned particle binding matter infiltrates a vesicular structure object, and it hydrolyzes on this coat, and heats and creates on it.

[0044] Next, the opening of the vesicular structure object which put the solid electrolyte 3 is filled up with a negative-electrode active material, and an electrode 4 is formed in it. The fine particles of a negative-electrode active material are infiltrated into the opening of an electrode 2 with the quality of packing, and the restoration object used as the other poles of a solid electrolyte cell is produced. Although it is desirable from the point of the volume energy density of a charge-and-discharge operation that these structures can be formed by restoration of a restoration object so that a filling factor may become about 100%, it is not limited to this.

[0045] as restoration matter of this negative electrode, the ion conductivity matter, the lithium content matter, the dielectric matter, etc. are desirable, dielectric matter, such as an organic solvent, etc. is mentioned and oxides of the metal alkoxide by the sol-gel method, such as low melting glass of the presentation containing lithiums, such as a crystallization glass [which specifically has ion conductivity], amorphous glass, and organic giant molecule, a gel electrolyte, and nonaqueous electrolyte, etc. are independent in these -- or it can mix and use. For example, ion conductivity glass ceramics have the high melting point, and since there is a possibility of destroying the crystal structure of an active material and causing trouble to an oxidation reduction reaction when the temperature of active material fine particles goes up by high binding temperature, it is good to mix and use the organic macromolecule which can more specifically perform low-temperature binding as quality of packing.

[0046] Moreover, if an electronic conduction nature grant matter particle is mixed and used for an active material particle when an active material particle is bound qualitatively of packing, and it considers as a restoration object, and the electronic conduction nature of this restoration object is small and inadequate, electronic conduction nature can be improved and electronic migration resistance can be made small.

[0047] Active material fine particles, quality of packing, etc. can be made liquefied (the shape of a slurry) with a solvent etc., this packing structure is infiltrated, and it dries to a porous body, and it can calcinate and create them to it. The smaller one of the size of the sinking-in particle which forms an electrode 4 is better than the size of the frame particle which forms an electrode 2 from a viewpoint of raising the amount of sinking in (filling factor). Moreover, it can form at low temperature more and the way of the quality of packing which does not produce the evaporation matter at the time of baking can raise a filling factor.

[0048] By the way, as an ingredient of a negative-electrode active material, lithium content transition-metals oxide (transition metals are one or more kinds), such as carbon system ingredients, such as a metal lithium, a lithium alloy, a graphite, and corks, a lithium titanate-acid ghost, lithium cobalt oxide, a lithium nickel oxide, a lithium manganate acid ghost, a lithium nickel manganate acid ghost, a lithium iron manganate acid ghost, or a lithium vanadate san ghost, a manganese dioxide, 5 niobium oxide, a lithium transition-metals compound nitride, or TiS_2 is mentioned, for example.

[0049] Moreover, as electronic conduction nature grant matter used with a negative-electrode active material, metallic oxides, such as carbon, acetylene black, and ITO, SnO , etc. are mentioned. What is necessary is just to replace a negative-electrode active material at the above-mentioned positive active material in the case of a positive electrode, although the case where the electrode of packing structure was a negative electrode was mentioned here.

[0050] Next, the negative-electrode (or positive electrode) charge collector 5 is formed in the cell cell confrontation of a charge collector 1. Various approaches can be considered as the formation approach and it is not limited to the following forming methods. For example, the film of electronic conductivity etc. is formed in the restoration electrode 4 by vacuum deposition, the sputtering method, spreading, baking of conductive paste, etc.

[0051] In drawing 2, an interlayer may be prepared between an electrode 2, a solid electrolyte 3, and an electrode 4 and a solid electrolyte 3, as for such an interlayer, it is desirable to carry out natural formation at the reaction by process temperature, and, generally he becomes a middle

presentation in presentation.

[0052] In drawing 2 , by sinking nonaqueous electrolyte, such as an organic solvent or an organic solvent, and lithium salt, into all the configuration layers of an electrode 2, a solid electrolyte 3, and an electrode 4, few openings (defect) included especially in an electrode 4, a solid electrolyte 3, and an electrode 2 can be filled, and the result of still better current density is obtained. As an organic solvent, there are PC (propylene carbonate), NMP (N-methyl-2-pyrrolidone), etc. Moreover, there is LiBF₄ etc. as lithium salt which sinks in.

[0053] By carrying out the laminating of the more than one, the generation-of-electrical-energy cel of this invention can raise a generation-of-electrical-energy electrical potential difference, or can increase a generation-of-electrical-energy current.

[0054] What is necessary is for the metal lead linked to charge collectors 1 and 5 etc. to be sufficient as these electrode terminals, and just to form a protective coat or a sheathing object in drawing 1 , so that a metal lead may not be covered and the peripheral face of a solid electrolyte cell may be covered although forward and negative the electrode terminal, protective coat, or sheathing object of a solid electrolyte cell was not illustrated. Thereby, permeation of the moisture to a solid electrolyte cell etc. can be inhibited. As a protective film object, moisture-proof *****/or the sealing agents for being airtight, such as protection resin, inorganic glass, etc. for semiconductor chips, are mentioned. As a protection sheathing object, since electric insulation and fanciness are given to the outside section, the laminate film which laminated the metal sheet with insulating polyethylene terephthalate (PET), polyethylene (PE), etc. can be used.

[Translation done.]

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EXAMPLE

[Example] Flat-surface size produced the solid electrolyte cell as the cross-section configuration shows to drawing 1 by 20mmx20mm.

[0056] The low melting glass ($\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{ZnO}$) which has a lithium titanate-acid ghost ($\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}\text{O}_4]$) as a negative-electrode active material, and has lithium ion conductivity as particle binding matter to 85% of the weight was mixed 15% of the weight. To this mixture, the binder (polyvinyl butyral) was added and the paste was adjusted for toluene to the solvent. Sheet forming of the adjusted paste was carried out so that thickness might be set to 200 micrometers with a doctor blade. After drying this, it sintered at 650 degrees C and the porous body electrode was created.

[0057] Au was vapor-deposited in thickness of 0.5 micrometers with vacuum evaporation equipment, and the negative-electrode charge collector was formed in one side of this porous body electrode.

[0058] Next, toluene and viscosity control were performed and pulverized coal of low melting glass ($\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{ZnO}$) which has lithium ion conductivity as a solid electrolyte was used as the solution. After sinking in and drying this adjusted solution to a porous body electrode, it calcinated at 500 degrees C. Short prevention was performed by thinning solution viscosity and repeating coat formation several times.

[0059] Next, acetylene black was mixed as an additive which makes electronic conductivity give a lithium manganate acid ghost ($\text{Li}[\text{Li}_{0.1}\text{Mn}_{1.9}\text{O}_4]$) to 80% of the weight as positive active material, and PVdF (polyvinylidene fluoride) was mixed 10% of the weight as 10 % of the weight and particle binding matter. To this mixture, addition mixing of the NMP (N-methyl-2-pyrrolidone) was carried out, and the paste for positive-electrode formation was adjusted. The adjusted solution was sunk in and dried to the above-mentioned porous body electrode, and the restoration electrode was created.

[0060] Next, Au was vapor-deposited in thickness of 0.5 micrometers with vacuum evaporation equipment, and the positive-electrode charge collector was formed in the field of this restoration electrode.

[0061] About this cell, when asked for the discharge current consistency, 11microA/cm² was obtained. Moreover, the utilization factor of charge and discharge was 20%.

As [the object for a comparison], next an object for a comparison, by 20mmx20mm, the cross section produced [flat-surface size] the solid electrolyte cell, as shown in drawing 3 .

[0062] The low melting glass ($\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{ZnO}$) which has a lithium titanate-acid ghost ($\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}\text{O}_4]$) as a negative-electrode active material, and has lithium ion conductivity as particle binding matter to 85% of the weight was mixed 15% of the weight. To this mixture, the binder (polyvinyl butyral) was added and the paste was adjusted for toluene to the solvent. Sheet forming of the adjusted paste was carried out with the doctor blade. After drying this, it sintered at 700 degrees C and the more precise negative electrode 2 whose thickness is 90 micrometers was created.

[0063] Next, the fine particles of the crystallization glass ($\text{Li}_2\text{O}-\text{SiO}_2$, $\text{Li}_2\text{O}-\text{SiO}_2-\text{P}_2\text{O}_5$) of lithium ion conductivity and the fine particles of the low melting glass ($\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{ZnO}$) which has lithium ion conductivity were adjusted with toluene as a solid electrolyte 3, and it considered

as the paste. After printing this adjusted paste to the above-mentioned negative electrode and drying, it calcinated at 550 degrees C and the solid electrolyte 3 with a thickness of 20 micrometers was obtained.

[0064] Next, after mixing acetylene black as an additive which makes electronic conductivity give a lithium manganic acid ghost ($\text{Li}[\text{Li}_{0.1}\text{Mn}_{1.9}\text{O}_4]$) to 80% of the weight as positive active material and mixing PVdF (polyvinylidene fluoride) 9% of the weight as 11 % of the weight and restoration matter, addition mixing of the NMP (N-methyl-2-pyrrolidone) was carried out, and the paste for positive-electrode formation was adjusted to this mixture. After printing the adjusted paste to the above-mentioned layered product and drying, it calcinated at 500 degrees C and the positive electrode with a thickness of 90 micrometers was created.

[0065] Next, Au was vapor-deposited in thickness of 0.5 micrometers with vacuum evaporationo equipment, respectively, and the negative electrode and the positive-electrode charge collector were formed in both sides of this negative electrode and a positive electrode.

[0066] When asked for the discharge current consistency about this cel, 1microA/cm² was obtained. Moreover, the utilization factor of charge and discharge was 2%.

[0067] Conventionally, to the example of a comparison of structure, the discharge current consistency of this invention article improved from 1microA/cm² to 11microA/cm², and the utilization factor of charge and discharge improved from 2% to 20% in connection with this.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the sectional view showing the solid electrolyte cell concerning this invention.

[Drawing 2] It is the important section sectional view showing the solid electrolyte cell concerning this invention.

[Drawing 3] It is the sectional view showing the conventional solid electrolyte cell.

[Description of Notations]

1: A positive-electrode charge collector, 2:positive electrode, 3:solid electrolyte, 4:negative electrode, 5 : negative-electrode charge collector

[Translation done.]

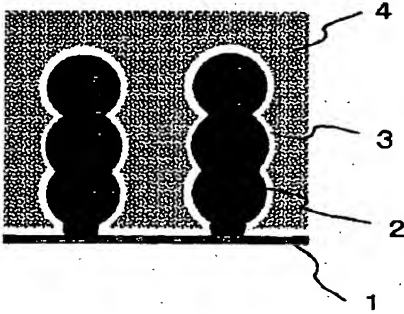
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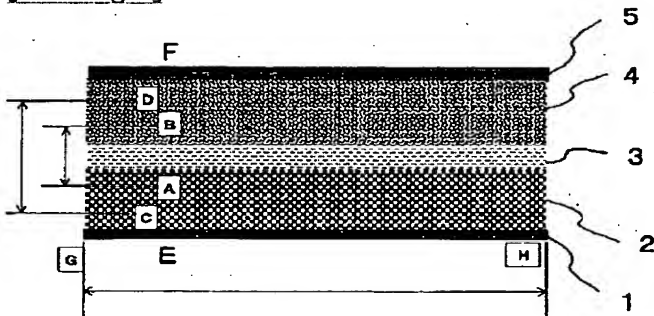
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DRAWINGS

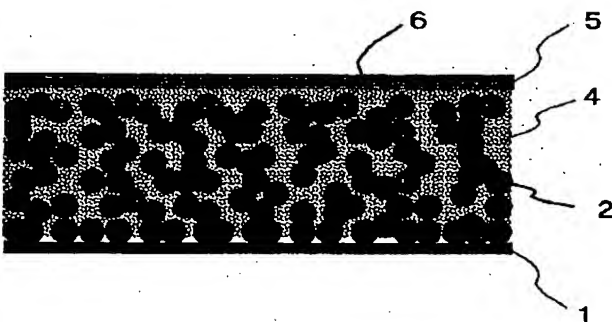
[Drawing 2]



[Drawing 3]



[Drawing 1]



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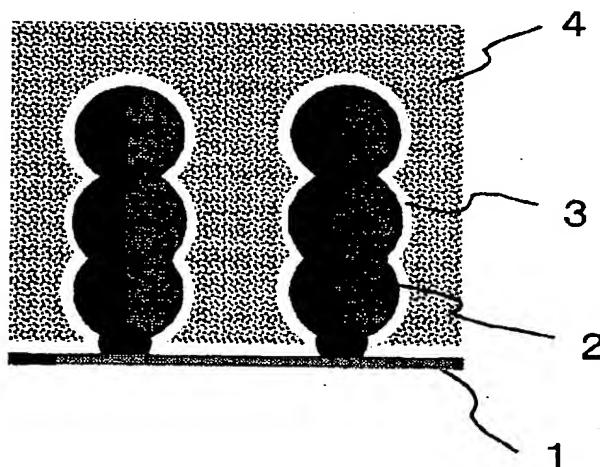
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(54) 【発明の名称】 固体電解質電池およびその製造方法

(57) 【要約】

【課題】 固体電解質の内部抵抗が高く、充放電電流や充放電容量を小さいという問題があった。

【解決手段】 活物質と粒子結着物質との多孔質構造体から成る一極性側電極と、この多孔質構造体の空隙部表面に被着したイオン伝導性物質から成る固体電解質層と、この多孔質構造体の空隙部に充填された他の活物質と充填物質とから成る他の極性側電極とを有し、上記一極性側電極と他の極性側電極に集電体を設けた。



【特許請求の範囲】

【請求項 1】 活物質と粒子結着物質との多孔質構造体から成る一極性側電極と、この多孔質構造体の空隙部表面に被着したイオン伝導性物質から成る固体電解質層と、この多孔質構造体の空隙部に充填された他の活物質と充填物質とから成る他の極性側電極とを有し、前記一極性側電極と他の極性側電極に集電体を設けた固体電解質電池。

【請求項 2】 前記多孔質構造体の活物質に電子伝導性付与物質が添加されていることを特徴とする請求項 1 に記載の固体電解質電池。

【請求項 3】 前記粒子結着物質が前記イオン伝導性物質および／または誘電物質からなることを特徴とする請求項 1 に記載の固体電解質電池。

【請求項 4】 前記イオン伝導性物質が結晶化ガラス、低融点ガラス、および高分子のうちのいずれか一種または複数種からなることを特徴とする請求項 1 または請求項 3 に記載の固体電解質電池。

【請求項 5】 前記誘電物質が低融点ガラスおよびゾルーゲル法による金属アルコキシドの酸化物のうちのいずれか一種または複数種からなることを特徴とする請求項 3 に記載の固体電解質電池。

【請求項 6】 前記固体電解質層に前記粒子結着物質が添加されていることを特徴とする請求項 1 に記載の固体電解質電池。

【請求項 7】 前記他の極性側電極の他の活物質に前記電子伝導性付与物質が添加されていることを特徴とする請求項 1 に記載の固体電解質電池。

【請求項 8】 前記充填物質がイオン伝導性物質および／または誘電物質からなることを特徴とする請求項 1 に記載の固体電解質電池。

【請求項 9】 前記イオン伝導性物質が結晶化ガラス、低融点ガラス、高分子、ゲル、および非水電解液のうちのいずれか一種または複数種からなることを特徴とする請求項 8 に記載の固体電解質電池。

【請求項 10】 前記誘電物質が低融点ガラス、ゾルーゲル法による金属アルコキシドの酸化物、および有機溶媒のうちのいずれか一種または複数種からなることを特徴とする請求項 8 に記載の固体電解質電池。

【請求項 11】 粒子結着剤と有機バインダーを含有する活物質粉体の生成形体を焼成して多孔質構造体を形成し、粒子結着剤を含有する固体電解質粉体を溶媒で粘液状にして前記多孔質構造体に含浸させて焼成して前記多孔質構造体の空隙部表面に固体電解質層を被着し、さらに充填物質を含有する他の活物質粉体を溶媒で粘液状にして前記多孔質構造体の空隙部に充填して焼成する固体電解質電池の製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は固体電解質電池とそ

の製造方法に関し、特に電極の内部抵抗の低減化を図って充放電電流や充放電容量を向上させた固体電解質電池とその製造方法に関する。

【0002】

【従来の技術】 電極の電気化学反応を利用した素子には、従来、液系やゲル系のものがある。例えば非水電解液リチウムイオン電池においては、正極集電体に正極活物質を塗布した正極と、負極集電体に負極活物質を塗布した負極とをセパレータを介して積層し、この積層体に有機溶媒とリチウム塩からなる高いイオン伝導性の電解液を含浸させて、電極と電解質の界面で良好なイオンの移動を起こさせ、また正・負電極の活物質と電解液の界面では酸化・還元反応と共に電子やイオンの良好な移動を起こさせ、実使用レベルの電池特性が得られている。これは液系電解質の濡れ性のよさと高いイオン伝導性によって可能となっており、ゲル系電解質についてもほぼ同様の理由で実使用レベルの特性が得られている。液系やゲル系の電解質電池をさらに改善する試みとして以下の例がある。

【0003】 特開平 10-223207 号 (①) によれば、上記と同様の非水電解液二次電池において、正極および負極の少なくとも一方に凹凸部を形成して表面積を拡大することにより、電池の電流容量を拡大すると共に、電池の電流負荷特性を改善し、過充電されたり過大な電流で放電しても、性能劣化を招く恐れが無くなったとしている。また、本公報によれば、負荷特性を改善する従来例として、低粘度溶媒系の採用と並んで、電極の厚みを薄くすると同時に、長さを長くすることによって電気化学的反応に寄与する表面積を増加させて、二次電池の負荷特性を改善する例を上げている。しかし、電極の長さの増加に伴って電気化学的反応に寄与しない集電体などが占める体積の割合も増加することになり、単位体積当たりの電池容量が減少する。

【0004】 特開平 11-162519 号 (②) によれば、従来のリチウムイオン二次電池では、ペレット状の正極、負極の反応面がセパレータと接する部分に限られているため、全体の活物質を反応に寄与させることができず、正極活物質の重量から求められる理論容量が得られず、また正極、負極とセパレータとの接触面積が十分でなく、電池の内部抵抗が高くなるという問題があった。そこで、正極および負極の表面に凹凸を形成し、この凹凸が互いに噛み合うようにセパレータを介して正極と負極を対向配置することで、接触面積を増加させて内部抵抗の低減および容量の向上を図ることができたとしている。他方、安全性、小型化、広い使用温度範囲、あるいは使い勝手のよさなどに対する要望が近年高まり、素子の全固体化を検討し、固体電解質の従来例をあげている。

【0005】 特開平 5-109429 号 (③) によれば、無機酸化物からなる電子伝導体層とイオン伝導体層

とを有する積層体において、両層の界面を凹凸状に接触させることにより、その界面の表面積を拡大して反応効率を向上させ、電極反応における電子やイオンの移動が良好になったとしている。

【0006】特開平9-180705号(4)によれば、活物質または活物質と導電剤との混合粉末が高分子固体電解質やゲル電解質と直接に接触した固体状電極を有するリチウム電池の正極および負極では、活物質粒子と高分子固体電解質やゲル電解質との接触が悪く、界面のインピーダンスが高いという欠点があったため、活物質粒子の表面に濡れ性のよいポリビニルピリジンと電解質の層を形成して、この粒子の空隙に電解質を充填することにより、活物質粒子同士の密着性を向上させると共に、電池の容量を向上させ、安定したサイクル性が得られたとしている。

【0007】

【発明が解決しようとする課題】本発明は、液系の従来例①②の課題と固体系の従来例③④の課題をより効果的に改善するとともに、例えば電極マトリックスや電解質の物性がイオン伝導度の小さい固体電解質であっても、これを補う構造を提案することを目的とする。

【0008】従来例①～③では、シート形状の電極および電解質を積層した形で、これらの断面は、図3に示すように、矩形を維持したまま電極2、4と電解質3の界面を凹凸にして接触面積の拡大を図ったものであり、接触面積の拡大に比例した界面抵抗の減少効果があると思われるが、その改善には限界がある。本発明の目的1はこの限界を超えることにある。

【0009】図3の従来例は、正電極2、負電極4、そして固体電解質3の断面形状はいずれも矩形(シート状、ペレット状)であり、一般的にはシート成形法などで作って積層して固体電解質電池とする。図3において、電極2と電極4は、それぞれ正極活物質粉体もしくは負極活物質粉体のいずれかと電子伝導性付与物質と固体電解質などから成る結着物質とで構成されている。図3によれば、電極2、4と固体電解質3との界面の接触面積は距離G-Hに比例する。上記した従来例①～③ではシート成形時に表面加工などして、電極2、4と固体電解質3の境界を波線や鋸歯状としたもので、この線分増に比例した界面抵抗の減少効果がある。

【0010】また、図3によれば、イオンあるいは電子が層間を移動する際、移動距離の違いによる移動抵抗の違いがある。正極活物質と負極活物質間、すなわちA-B間、C-D間とで比較した場合、この間をイオンが移動する距離は(A-B間) < (C-D間)であり、この間の移動抵抗は(A-B間) < (C-D間)であり、任意の正極活物質と負極活物質間の距離に比例した内部抵抗がある。図3の層厚は一般に電極が100μm前後で電解質が10μm前後である。従って、移動距離は10μmから200μmであり、平均的な移動距離は100

μm前後である。

【0011】また、イオンと電子とのキャリアの違いによる抵抗がある。また、液系と固体系との電解質の違いによる抵抗がある。イオンは、電子に比べ、サイズ・質量とも大きく、一般に固体中を高速で動くことは難しいが、非水電解液中では容易に高速で動くことができる。

【0012】リチウム塩を含む有機溶剤からなる非水電解液ではイオン伝導度が $1 \times 10^{-2} \sim 10^{-3} \Omega^{-1} \text{cm}^{-1}$ と大きく、このような移動距離の違いによる抵抗差は極めて小さく無視できる。一方、固体電解質3ではイオン伝導度が一般に $1 \times 10^{-4} \sim 10^{-6} \Omega^{-1} \text{cm}^{-1}$ と小さく、このような移動距離による抵抗は大きく、移動距離の違いによる抵抗差も極めて大きい。他方、電子は、電子がそれぞれの電極から集電体に移動する距離も、C-E、D-FとA-E、B-Fとで異なるが、電子本来の移動速度はイオンの移動速度に比べて早く、この移動距離による抵抗は小さく、移動距離の違いによる抵抗差も小さい。

【0013】しかし、例えば電極2、4における活物質の分量を増やすために、電子伝導性付与物質の分量を減らすと、電子伝導性付与物質が不十分になって、電極2、4内のマイクロ構造に乱れが発生し、電子伝導度が小さくなり、電子の移動距離による抵抗は大きくなり、移動距離の違いによる抵抗差も大きくなって、無視できなくなる。

【0014】従来例④では、電極活物質粉体とこれを囲むマトリックス状の固体電解質との接触界面(いわゆる粒界)抵抗の低減化を図っている。本発明ではこの粒界抵抗を低減する他の例をあげている。

【0015】従来例①～④にはない重要な課題がある。それは、固体電解質で構成された電極活物質粉体を囲む電極マトリックスと固体電解質層のバルク抵抗が大きいことである。これは固体電解質が液系やゲル系の電解質に比べ、イオン伝導度が小さいことに起因している。このため、正極活物質粉体から負極活物質粉体までのイオンの移動距離に比例した内部抵抗が大きく現れ、この抵抗に起因して、充放電電流密度が小さくなったり、正電極と負電極の反応面が固体電解質に接する領域に限られて活物質の利用率が低下し、充放電容量が小さくなるという問題があった。本発明の目的2はこの問題を解消することにある。

【0016】目的1では、イオンの移動は電極と電解質層との界面でも起こるため、この界面の表面積を従来例以上にできるだけ大きくすればよい。目的2では、電気化学素子の特性である化学反応(酸化還元反応)は活物質粉体とこれを囲む電解質との界面で起こるため、反応効率を挙げるにはこの粒界の表面積をできるだけ大きくすればよく、また正極活物質粉体から負極活物質粉体までのイオンの移動距離をできるだけ短くすればよい。

【0017】本発明は、電極の電気化学反応を利用した

電解質が固体のイオニクス素子、より具体的には固体電解質電池の新しい構造を提示するもので、これにより目的 1、2、すなわち電極と固体電解質層の界面抵抗、そして電解質のバルク抵抗に起因する正極活物質粉体から負極活物質粉体までのイオンの移動抵抗を低減することにある。そして付加的に、正極（もしくは負極）活物質粉体から正極（もしくは負極）集電体までの電子の移動抵抗も低減しようとするものである。本発明の最終的な目的は、これらの内部抵抗の低減化を図ることにより、固体電解質電池の充放電電流や充放電容量を向上させることにある。

【0018】

【課題を解決するための手段】請求項 1 に係る固体電解質電池は、活物質と粒子結着物質との多孔質構造体から成る一極性側電極と、この多孔質構造体の空隙部表面に被着したイオン伝導性物質から成る固体電解質層と、この多孔質構造体の空隙部に充填された他の活物質と充填物質とから成る他の極性側電極とを有し、前記一極性側電極と他の極性側電極に集電体を設けた。

【0019】上記固体電解質電池では、前記多孔質構造体の活物質に電子伝導性付与物質が添加されていることが望ましい。

【0020】上記固体電解質電池では、前記粒子結着物質が前記イオン伝導性物質および／または誘電物質からなることが望ましい。

【0021】上記固体電解質電池では、前記イオン伝導性物質が結晶化ガラス、低融点ガラス、および高分子のうちのいずれか一種または複数種からなることが望ましい。

【0022】上記固体電解質電池では、前記固体電解質層に前記粒子結着物質が添加されていることが望ましい。

【0023】上記固体電解質電池では、前記他の極性側電極の他の活物質に前記電子伝導性付与物質が添加されていることが望ましい。

【0024】上記固体電解質電池では、前記充填物質がイオン伝導性物質および／または誘電物質からなることが望ましい。

【0025】また、請求項 1 に係る固体電解質電池の製造方法では、粒子結着剤と有機バインダーを含有する活物質粉体の生成形体を焼成して多孔質構造体を形成し、粒子結着剤を含有する固体電解質粉体を溶媒で粘液状にして前記多孔質構造体に含ませて焼成して前記多孔質構造体の空隙部表面に固体電解質層を被着し、さらに充填物質を含有する他の活物質粉体を溶媒で粘液状にして前記多孔質構造体の空隙部に充填して焼成することとを特徴とする。

【0026】

【発明の実施の形態】図 1 は本発明に係る固体電解質電池の断面を示す模式図である。図 2 は図 1 の断面の要部

を拡大した図である。

【0027】図 1 および図 2 において、1 は一極性側（正極もしくは負極）集電体、2 は一極性側（正もしくは負）電極、3 は固体電解質層、4 は他の極性側（負もしくは正）電極、5 は他の極性側（負極もしくは正極）集電体である。以下、便宜上、一極性側を正、他の極性側を負として説明する。図 1 および図 2 と図 3 の違いは、正電極、負電極、そして固体電解質の断面形状である。

【0028】図 1 において、多孔質構造体を骨格とした正電極 2 の断面形状は大きい粒子の集まりのぶどう房状に模式的に図示しており、負電極 4 の断面形状は小さい粒子の集まりで、上記ぶどう房状の隙間を埋めるように模式的に図示しており、固体電解質 3 の断面形状はこれら正電極 2 の断面と負電極 4 の断面の境界に一定の薄い厚みを成しており、図 1 の要部拡大図である図 2 に模式的に図示する薄層である。

【0029】ぶどう房状の正電極 2 は、電子伝導性とイオン伝導性において導通状態である。電子的には集電体 1 にも接続状態である。また、図 1 に孤立したぶどう房状の断面部 6 が図示されているが、他の切り口ではぶどう房状の正電極 2 に繋がっており、いずれも多孔質電極の一部である。

【0030】図 1 において、正電極 2 は正極活物質粉体と粒子結着物質とで構成され、この他に電子伝導性物質を含んでもよい。また、固体電解質 3 はイオン伝導性を有し、粒子結着物質などで構成されている。また、負電極 4 は負極活物質粉体と充填物質とで構成され、この他に電子伝導性物質を含んでもよい。図 1 の集電体 1、5 を除いた厚みは、図 3 とほぼ同等の活物質を保有する意味で 200 μm 前後とする。

【0031】この図 1 を基に、イオンと電子のそれぞれについて、正極 2 と負極 4 間の移動距離を考察すると、電極 2、4 のどの箇所においても、それは多孔質構造体である正電極 2 のぶどう房状の粉体粒の大きさ程度、あるいは多孔質体を埋めるように充填された負電極 4 の粉体粒の大きさ程度、すなわち高々数 μm であることが図より明らかである。

【0032】この程度の小さな移動距離であれば、例えば電極 2、4 内のイオン伝導性や電子伝導性が小さくても、移動距離に起因するイオン抵抗や電子抵抗は非常に小さい。また、固体電解質 3 の厚みも薄く、固体電解質 3 内のイオン抵抗も小さい。さらに、電極 2、4 と集電体 1、5 との移動距離に伴う電子伝導性についても、電極 2、4 内で高い電子伝導性が確保されていれば、電子抵抗は小さく無視できる。すなわち、固体系が液系に比べてイオンや電子の抵抗率が例え 2 桁大きくても、本発明によれば移動距離が 2 桁程度小さくできるため、イオンや電子の移動抵抗はほぼ同じ抵抗にできる。また、電極 2、4 と固体電解質 3 との界面の面積は、図 1 より容

易に推察できるように飛躍的に増大する。したがって、電極 2、4 と固体電解質 3 との界面の抵抗も激減できる。

【0033】このように電極 2、4 と固体電解質 3 の層厚がそれぞれ薄く、充放電電流密度が広い層面において均一であり、例えば電流密度が小さくても広い層面により、全体の電流としての充放電電流密度（この密度は集電体 1、5 に対する単位面積当たりである）は大きくなり、充放電容量も大きくなる。

【0034】図 1 および図 2 に示すような構造の固体電解質電池を形成するには様々な方法がある。

【0035】まず、正極活物質から成る多孔質構造体の電極 2 を作製する。正極活物質の粉体を粒子結着物質で結着して、固体電解質電池の骨格となる多孔質体を作製する。多孔質体の充填率は 50% 以下が充放電作用の利用率から好ましいがこれに限定されるものではない。

【0036】粒子結着物質としては、イオン伝導性物質やリチウム含有物質や誘電物質などが好ましく、例えばイオン伝導性を有する結晶化ガラス、非晶質ガラス、有機高分子など、あるいはリチウムを含有する組成の低融点ガラスなど、あるいはゾルーゲル法による金属アルコキシドの酸化物などが挙げられ、これらを単独もしくは混合して利用できる。例えば、イオン伝導性の結晶化ガラスは融点が高く、高い結着温度で活物質粉体の温度が上がると活物質の結晶構造を破壊して酸化還元反応に支障をきたす恐れがあるので、より具体的には粒子結着物質として低温結着ができる低融点ガラスなどを混合して用いるのがよい。

【0037】また、活物質粒子を粒子結着物質で結着して多孔質体としたとき、この多孔質体の電子伝導性が小さくて不十分な場合、活物質粒子に電子伝導性付与物質粒子を混合するなどして用いると電子伝導性が高くできて電子の移動抵抗が小さくできる。

【0038】この多孔質構造体は、活物質粉体と粒子結着物質粉体などを溶媒や有機バインダーなどとともに粘液状（スラリー状）とし、ドクターブレードでシート成形など行い、乾燥し、焼結させて作成できる。成形に用いた有機バインダーなどを焼成して飛ばし、多孔質構造体の空隙を作ることができる。ドクターブレード法の他に印刷法や浸漬法がある。また、この多孔質構造体は、活物質粉体などを金属アルコキシドと混合して液状（スラリー状）とし、シート成形など行って乾燥して作成できる。乾燥時に、アルコール成分が気化して、多孔質構造体の空隙を作ることができる。

【0039】より具体的には、粒子結着物質として、PVdF（ポリ弗化ビニリデン）、PEO（ポリエチレンオキシド）、水酸化リチウム、炭酸リチウム、りん酸リチウム、また、 $\text{Li}_2\text{O}-\text{SiO}_2$ 、 $\text{Li}_2\text{O}-\text{SiO}_2-\text{P}_2\text{O}_5$ などのリチウム含有金属酸化物（金属は一種以上）、 $\text{Li}_2\text{P}_2\text{O}_7$ 、 N_x などのリチウム含有金属窒化

物、 TiS_2 、あるいは $\text{Li}_2\text{S}-\text{SiS}_2-\text{LiI}$ などのリチウム含有金属硫化物、リチウムチタン酸化物などのリチウム含有遷移金属酸化物などが挙げられる。これらを単独あるいは混合して用いる。

【0040】正極活物質の材料としては、例えばリチウムコバルト酸化物、リチウムニッケル酸化物、リチウムマンガン酸化物、リチウムニッケルマンガン酸化物、リチウムチタン酸化物、リチウム鉄マンガン酸化物、あるいはリチウムバナジウム酸化物などのリチウム含有遷移金属酸化物（遷移金属は一種以上）、また二酸化マンガ、五酸化ニオブ、リチウム遷移金属複合窒化物、 TiS_2 、あるいは $\text{V}_2\text{O}_5-\text{P}_2\text{O}_5$ などが挙げられる。

【0041】また、電子伝導性付与物質としては、カーボン、アセチレンブラック、ITO、 SnO_2 などの金属酸化物などが挙げられる。ここでは、多孔質構造体の電極が正極 2 の場合を挙げたが、これが負極 4 の場合には後述の負極活物質に置きかえればよい。

【0042】次に、正極集電体 1 を正電極 2 の一面に形成する。形成の方法としては様々な方法がある。例えば多孔質構造体の電極 2 の少なくとも一面に電子伝導性の膜など（Au や Ag や Al や Cu など）を蒸着法やスパッタリング法で形成したり、導電ペースト（Au や Ag や Al や Cu 粒子を樹脂に混合したもの）を塗布して焼成することにより形成する。その他の形成方法としては、ニッケル、ステンレス、アルミニウム、銅、カーボンなどからなるシート状の金属箔を電子伝導性の粒子を混合した樹脂ペーストで電極に貼り合せて乾燥・焼成してもよい。

【0043】次に、得られた多孔質構造体の空隙部表面を電解質で被覆し、図 2 に示すような薄い固体電解質層 3 を形成する。このような固体電解質層 3 を形成するには、上記粒子結着物質のようなイオン伝導性を有するものが好適であり、このような粉体などを溶媒とともに粘液状（スラリー状）として、多孔質構造体中含浸させて、乾燥して作成する。また、この被膜には、上記粒子結着物質を用いずにゾルーゲル法による金属アルコキシドの酸化物などを形成できる溶液に多孔質構造体中含浸させて、加水分解して加熱して作成する。

【0044】次に、固体電解質 3 を被着した多孔質構造体の空隙に、負極活物質を充填して電極 4 を形成する。負極活物質の粉体を充填物質とともに電極 2 の空隙に含浸させ、固体電解質電池の他極となる充填体を作製する。充填体の充填により、これらの構造体は充填率が 100% 近くになるように形成できるのが充放電作用の体積エネルギー密度の点から好ましいが、これに限定されるものではない。

【0045】この負極の充填物質としては、イオン伝導性物質やリチウム含有物質や誘電物質などが好ましく、具体的にはイオン伝導性を有する結晶化ガラス、非晶質ガラス、有機高分子、ゲル電解質、非水電解液など、あ

るいはリチウムを含有する組成の低融点ガラスなど、あるいはゾルーゲル法による金属アルコキシドの酸化物など、あるいは有機溶媒などの誘電物質などが挙げられ、これらを単独もしくは混合して利用できる。例えばイオン伝導性の結晶化ガラスは融点が高く、高い結着温度で活物質粉体の温度が上がると活物質の結晶構造を破壊し、酸化還元反応に支障をきたす恐れがあるので、より具体的には充填物質として低温結着ができる有機高分子などを混合して用いるのがよい。

【0046】また、活物質粒子を充填物質で結着して充填体としたとき、この充填体の電子伝導性が小さくて不十分な場合、活物質粒子に電子伝導性付与物質粒子を混合して用いると、電子伝導性を改善でき、電子の移動抵抗を小さくできる。

【0047】この充填構造は、活物質粉体と充填物質などを溶媒などとともに液状（スラリー状）とし、多孔質体に含浸させ、乾燥し、焼成して作成できる。電極4を形成する含浸粒子のサイズは、電極2を形成する骨格粒子のサイズより含浸量（充填率）を高めるという観点から、より小さいほうがよい。また、より低温で形成でき、焼成時に気化物質を生じない充填物質のほうが充填率を高めることができる。

【0048】ところで、負極活物質の材料としては、例えば金属リチウム、リチウム合金、黒鉛やコークスなどの炭素系材料、リチウムチタン酸化物、リチウムコバルト酸化物、リチウムニッケル酸化物、リチウムマンガン酸化物、リチウムニッケルマンガン酸化物、リチウム鉄マンガン酸化物、あるいはリチウムバナジウム酸化物などのリチウム含有遷移金属酸化物（遷移金属は一種以上）、二酸化マンガ、五酸化ニオブ、リチウム遷移金属複合窒化物、あるいは $TiSi_2$ などが挙げられる。

【0049】また、負極活物質とともに用いられる電子伝導性付与物質としては、カーボン、アセチレンブラック、ITO、 SnO などの金属酸化物などが挙げられる。ここでは充填構造の電極が負極の場合を挙げたが、正極の場合には負極活物質を前述の正極活物質に置きかえればよい。

【0050】次に、負極（もしくは正極）集電体5を集電体1の電池セル対面に形成する。形成方法としては、様々な方法が考えられ、以下の形成法に限定されるものではない。例えば充填電極4に電子導電性の膜などを蒸着法やスパッタリング法や導電ペーストの塗布・焼成などにより形成する。

【0051】図2において、電極2と固体電解質3、および電極4と固体電解質3との間に中間層を設けてもよく、このような中間層はプロセス温度による反応で自然形成するのが好ましく、組成的には一般に中間組成となる。

【0052】図2において、電極2と固体電解質3、および電極4の全構成層に有機溶媒あるいは有機溶媒とリ

チウム塩などの非水電解液を含浸することにより、特に電極4、固体電解質3、および電極2に含まれる僅かな空隙（欠陥）を満たすことができ、さらにより電流密度の結果が得られる。有機溶媒としては、PC（プロピレンカーボネート）、NMP（N-メチル-2-ピロリドン）などがある。また含浸するリチウム塩としては $LiBF_4$ などがある。

【0053】本発明の発電セルは、複数個積層することで、発電電圧を高めたり、発電電流を増すことができる。

【0054】図1では、固体電解質電池の正・負の電極端子や保護膜あるいは外装体は図示しなかったが、これらの電極端子は集電体1、5に接続した金属リードなどでよく、保護膜あるいは外装体は金属リードを被覆しないように固体電解質電池の外周面を覆うように形成すればよい。これにより固体電解質電池への水分の浸入などを抑止することができる。保護皮膜体としては半導体チップ用の保護樹脂や無機ガラスなど、耐湿および／または気密のための封止材が挙げられる。保護外装体としては、外面部に電気的絶縁性や装飾性を持たせるため、絶縁性のポリエチレンテレフタレート（PET）やポリエチレン（PE）などで金属シートをラミネートしたラミネートフィルムなどが使用できる。

【0055】

【実施例】平面サイズが $20\text{mm} \times 20\text{mm}$ でその断面形状が図1に示すような固体電解質電池を作製した。

【0056】負極活物質としてリチウムチタン酸化物（ $Li_{1/3}Ti_{2/3}O_2$ ）を85重量%に粒子結着物質としてリチウムイオン伝導性を有する低融点ガラス（ $Li_2O-B_2O_3-ZnO$ ）を15重量%混合した。この混合物に対して、バインダー（ポリビニルブチラール）を添加し、トルエンを溶剤にペーストの調整を行った。調整したペーストをドクターブレードで厚さが $200\mu\text{m}$ となるようにシート成形した。これを乾燥した後、 650°C で焼結し、多孔質体電極を作成した。

【0057】この多孔質体電極の片面に、蒸着装置でAuを $0.5\mu\text{m}$ の厚さに蒸着して負極集電体を形成した。

【0058】次に、固体電解質としてリチウムイオン伝導性を有する低融点ガラス（ $Li_2O-B_2O_3-ZnO$ ）の微粉体をトルエンと粘度調整を行って溶液とした。この調整した溶液を多孔質体電極に含浸して乾燥した後、 500°C で焼成した。溶液粘度を薄めて被膜形成を数回繰り返すことで、ショート防止を行った。

【0059】次に、正極活物質としてリチウムマンガン酸化物（ $Li_{0.4}Mn_{0.6}O_2$ ）を80重量%に、電子導電性を付与させる添加物としてアセチレンブラックを10重量%、および粒子結着物質としてPVdF（ポリフ化ビニリデン）を10重量%混合した。この混合物に対して、NMP（N-メチル-2-ピロリド

ン)を添加混合して正極形成用ペーストを調整した。調整した溶液を上記多孔質体電極に含浸して乾燥して充填電極を作成した。

【0060】次に、この充填電極の面に、蒸着装置でAuを0.5μmの厚さに蒸着して正極集電体を形成した。

【0061】このセルについて、放電電流密度を求めたところ、11μA/cm²が得られた。また、充放電の利用率は20%であった。

【比較用】次に、比較用として、平面サイズが20mm×20mmでその断面が図3に示すように固体電解質電池を作製した。

【0062】負極活物質としてリチウムチタン酸化物(Li[L_{1/3}Ti_{5/3}]O₄)を85重量%に粒子結着物質としてリチウムイオン伝導性を有する低融点ガラス(Li₂O-B₂O₃-ZnO)を15重量%混合した。この混合物に対して、バインダー(ポリビニルブチラール)を添加し、トルエンを溶剤にペーストの調整を行った。調整したペーストをドクターブレードでシート成形した。これを乾燥した後、700℃で焼結し、厚さが90μmのより緻密な負電極2を作成した。

【0063】次に、固体電解質3として、リチウムイオン伝導性の結晶化ガラス(Li₂O-SiO₂, Li₂O-SiO₂-P₂O₅)の粉体とリチウムイオン伝導性を有する低融点ガラス(Li₂O-B₂O₃-ZnO)の粉体をトルエンと調整を行ってペーストとした。この調整したペーストを上記負電極に印刷して乾燥した後、550℃で焼成して厚み20μmの固体電解質3を得た。

【0064】次に、正極活物質としてリチウムマンガン酸化物(Li[L_{0.1}Mn_{1.9}]O₄)を80重量%に、電子導電性を付与させる添加物としてアセチレンブラックを11重量%、および充填物質としてPVdF(ポリ弗化ビニリデン)を9重量%混合した後、この混合物にNMP(N-メチル-2-ピロリドン)を添加混合して正極形成用ペーストを調整した。調整したペーストを上記積層体に印刷して乾燥した後、500℃で焼成して厚み90μmの正電極を作成した。

【0065】次に、この負電極と正電極の両面に、蒸着*

*装置でAuをそれぞれ0.5μmの厚さに蒸着して負極および正極集電体を形成した。

【0066】このセルについて放電電流密度を求めたところ、1μA/cm²が得られた。また、充放電の利用率は2%であった。

【0067】従来構造の比較例に対し、本発明品は放電電流密度が1μA/cm²から11μA/cm²に向上し、これに伴って充放電の利用率は2%から20%に向上した。

【0068】

【発明の効果】以上のように、請求項1に係る固体電解質電池によれば、活物質の多孔質構造体から成る一極性側電極と、この多孔質構造体の空隙表面に被着したイオン伝導性物質から成る固体電解質層と、この多孔質構造体の空隙に充填された他の活物質から成る他の極性側電極とを有することから、固体電解質の高い内部抵抗を著しく軽減し、充放電電流や充放電容量を向上させることができる。

【0069】また、請求項11に係る固体電解質電池の製造方法によれば、粒子結着剤と有機バインダーを含有する活物質粉体の生成形体を焼成して多孔質構造体を形成し、粒子結着剤を含有する固体電解質粉体を溶媒とともに粘液状にして上記多孔質構造体中含浸させて焼成して多孔質構造体の空隙部表面に固体電解質層を被着し、さらに充填物質を含有する他の活物質粉体を溶媒とともに粘液状にして上記多孔質構造体の空隙に充填して焼成することから、固体電解質の高い内部抵抗を著しく軽減し、充放電電流や充放電容量を向上させた固体電解質電池を容易に製造できる。

【図面の簡単な説明】

【図1】本発明に係わる固体電解質電池を示す断面図である。

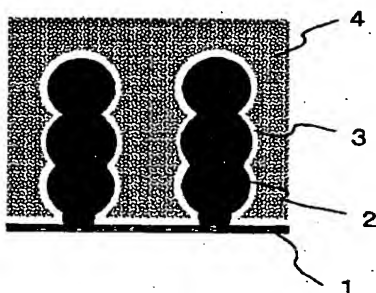
【図2】本発明に係わる固体電解質電池を示す要部断面図である。

【図3】従来の固体電解質電池を示す断面図である。

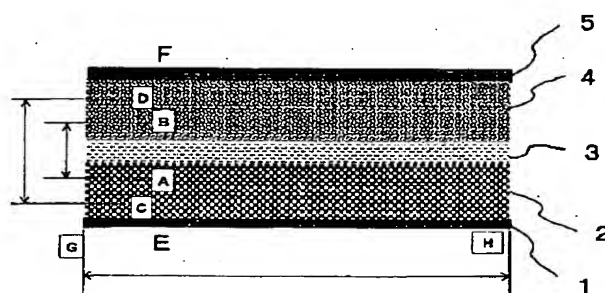
【符号の説明】

1：正極集電体、2：正電極、3：固体電解質、4：負電極、5：負極集電体

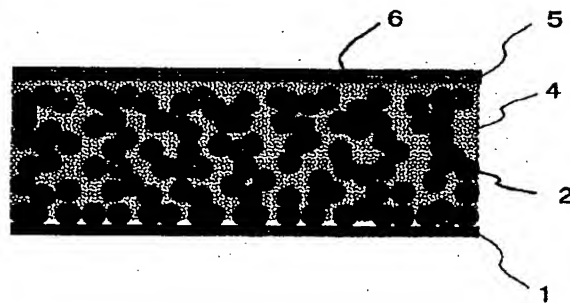
【図2】



【図3】



【図 1】



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